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American Leather Chemists Association

VOLUME XIV, 1919

PUBLISHED MONTHLY BY
THE AMERICAN LEATHER CHEMISTS
ASSOCIATION

THE CHEMICAL PUBLISHING CO., PRINTERS
EASTON, PA.

The Journal of the

American Leather Chemists Association

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Journal of the

American Leather Chemists Association

Vol. XIV JANUARY, 1919 No. 1

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Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $6.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized July 16, 1918.

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CHROME LEATHER PROBLEMS FOR RESEARCH LABORATORIES.

By E. J. White.

In recent discussion[1] on this subject, the point was somewhat overlooked that while it is advisable for a public research laboratory to confine its activities in the main to work of university type, it nevertheless remains to the interest of the individual manufacturer to maintain his own research laboratory qualified to engage in the same field. Private research laboratories are instituted for the purpose of following up manufacturing problems of abstruse or academic type, but they can at the same time very profitably and successfully study fundamentals which have no immediate industrial bearing. There is scope in the leather industry for all the public and private research which it can command, and it is with the object of illustrating the type of work that can be handed on to a research laboratory by chemists engaged in the chrome leather industry that the writer ventures to outline some comparatively definite problems.

1. *The Neutralization of Chrome Leather.*—The following observations apply to leather tanned by the two-bath process, using a second bath of sodium thiosulphate and hydrochloric acid.

Wet chrome leather can be shaken indefinitely with gradual additions of a dilute solution of caustic soda without reaching an end point when the residual liquor is permanently alkaline to phenolphthalein.

The problem is to separate the absorption of alkali into probably three components:

1. Neutralization of the acid introduced from the tanning baths.
2. Combination of alkali with skin substance.
3. Adsorption.

A method of isolating the first of the three components suggests itself in the analysis of the residual liquor for sodium salts. These salts turn out to be sulphate and thiosulphate, and can be readily measured by precipitation and titration respectively.

[1] This JOURNAL, 13, 239 and 397 (1918).

Application of this method of attack enables one to demonstrate the gradually diminishing proportion of alkali used in acid neutralization as more alkali is taken up, and gives a fair idea of the actual total acidity of the skin. It also shows that the initial proportion of the total neutralization is about 75 per cent. thiosulphate and 25 per cent. sulphate, indicating an apparent tannage by chromium salts of which 75 per cent. is basic chromium thiosulphate and 25 per cent. is basic chromium sulphate. The proportion of thiosulphate, however, gradually falls, so that after a few days standing in the wet condition the leather appears to be tanned with a salt that is 50 per cent. sulphate and 50 per cent. thiosulphate, and after long standing only sulphate is found. Moreover, the total acidity appears to be increasing.

The problems raised by these observations include the identification of chromium thiosulphate, and the group of questions connected with the form in which chromium is present in the leather, initially and after the leather has been standing some time. Another opening for study is given in the application of the boiling test on the leather before and after the neutralization. To stand boiling the chromium content must be above a certain limiting value, but the resistance to boiling is also affected by other factors, neutralization generally tending to increase the resistance. It remains to be proved, therefore, whether acid is present in the essential tanning agent or whether it is entirely a vehicle for the transference of chromium to the skin.

2. *The Dyeing and Fat-Liquoring of Chrome Leather.*—These processes can be studied, as was the neutralization, by the analysis of the residual liquors for sulphate and thiosulphate. In the case of direct dyes it is not surprising to find that the process is apparently one of further neutralization, the sulphonates of the dye reacting with the acid of the leather to liberate sodium sulphate and thiosulphate and deposit the sulphonic acid on the leather. There may perhaps be a question as to whether the sulphonic acid merely replaces the other acids, or whether there is real neutralization, the sulphonic acid being left only in physical attachment. The fact that dyeing increases the resistance to boiling is to some extent proof of the latter supposition.

In the analytical work a correction is usually needed for the

sodium sulphate present in the dyestuff as diluent. This can be estimated by adding dilute nitric acid to a small quantity of the dyestuff, when the diluents go into solution with the sulphonic acid left as residue. If the residue is collected on a tared filter, the total soluble diluent is thus determined, and the filtrate can be analyzed for individual materials. The procedure can also be modified to determine the approximate neutralizing power of a dyestuff, by using a measured amount of acid and then estimating what is left. Some complication is often caused by the necessity of washing the insoluble residue with water that is slightly acid to prevent the sulphonic acid going into colloidal solution.

Fat-liquoring, as far as the soap is concerned, turns out to be another process of neutralization, the acids of the leather being in this case displaced by fatty acids, which remain in all probability in a state of physical attachment.

3. *The Interference of Arsenic in Two-Bath Chrome Tannage.*—Originally brought to notice by Stiasny and Das,[2] it is probably widely known that the presence of a small amount of arsenic can violently disturb the proper reducing action of the thiosulphate bath. A simple test for the detection of small amounts of arsenic in commercial hydrochloric acid, in which arsenic is a common impurity, consists in the addition of potassium iodide solution to the undiluted acid; arsenic is indicated by a brown precipitate, presumably of arsenious iodide, which is dissolved at once on the addition of water.

The disturbing influence of arsenic can be demonstrated by adding thiosulphate solution to the acid containing it. With arsenic absent, the first additions of thiosulphate cause turbidity, while thiosulphate can be added in considerable quantity to acid containing a little arsenic without any immediate sign of turbidity though a precipitate of arsenic sulphide eventually appears.

4. *The Absorption of Chromic Acid from the First Bath.*—The first or bichromate bath of two-bath chrome tannage presents a fruitful field for chemical and physico-chemical study. The ordinary manufacturing process requires the employment of hydrochloric acid and bichromate, with the latter in large excess over

[2] This JOURNAL, 7, 508 (1912).

what would be equivalent to the hydrochloric acid. The necessity of this excess can be easily demonstrated, its omission resulting in incomplete absorption of chromic acid as well as a disadvantageous swollen condition of the skin. In no case is there evidence of the absorption of hydrochloric acid; the problem can therefore be simplified in initial investigation by using pure chromic acid and studying its absorption by the skin from various mixtures, giving due regard always to the alkalinity left in the skin from the unhairing processes.

In this connection, reference may be made to the absorption of acid from pickling baths. It can be easily demonstrated from determinations of the acidity and sulphate and chloride contents of spent pickle liquors that skins take up from the sodium chloride and sulphuric acid pickle not sulphuric acid but hydrochloric acid. Further study seems needed of the order of preferential absorption by skin of different acids.

The writer, in conclusion, expresses a hope with regard to the future publication of experimental work in which skin quantities are concerned. The corrections and approximations in such work are all-important details, and without exceptional pains being taken to explain them, the presentation of rows of tabulated figures must remain valueless. Broad vision is required of the limits of quantitative observation in a field where simplicity at present is mainly an empirical simplicity.

AN INVESTIGATION OF THE RELATIVE AFFINITY FOR COTTON, AND MORDANTING VALUE OF THE TANNINS OF GALLS, SUMAC, MYROBALANS, DIVI-DIVI, AND QUEBRACHO.

By Roy H. Wisdom.

Representative samples of known purity of gall, sumac, myrobalan, and quebracho extracts and divi-divi in the raw material were selected and analyzed for tannin content according to the Official Method of the American Leather Chemists' Association, with the following results:

	Galls	Sumac	Myrobalans	Divi-divi	Quebracho
Total solids	32.01	48.38	42.74	70.48	48.36
Soluble solids	31.69	47.90	41.29	63.90	44.75
Insolubles	0.32	0.48	1.45	6.58	3.61
Non-tannins	7.26	21.74	16.06	23.55	4.83
Tannins	24.43	26.16	25.23	40.35	39.92

Solutions were then made up, each containing exactly 0.4 gram tannin per 100 cc. The solutions were allowed to cool, and then 250 cc. of each were added to a quart bottle, together with 10 grams of washed and air-dried pure cotton cloth. The bottles were tightly stoppered, placed in a water bath of 160° F. for 30 minutes with frequent shaking, and then placed in a shaking machine and drummed for 1 hour. These solutions were then filtered through small No. 590 S. & S. filters and 100 cc. of the filtrate collected and evaporated to constant weight. At the same time, the full tannin analysis was repeated on the solutions before the addition of the cotton.

The returns showed the following absorption figures, based on the tannin percentage as returned by the Official A. L. C. A. Method:

TABLE I.

Material	Per cent. of matter absorbed by cotton
Galls	25.3
Sumac	27.1
Myrobalans	22.3
Divi-divi	18.1
Quebracho	17.3

As is noted, the above figures represent the amount of "matter" absorbed by cotton which is not necessarily synonymous with tannin. No doubt a full assay of the solution after absorption by cotton would prove more or less non-tannin absorption, but

inasmuch as the hide powder method returns as tannin all "matters absorbable by hide under the conditions of the prescribed methods" which undoubtedly includes certain amounts of the natural coloring matters allied to tannins, this procedure would be of little practical value, as the textile colorist is interested in the relative affinity for cotton of the various tanning material for what they actually give up to it, regardless as to whether it is true tannin in the chemical sense of the word or not. Accordingly a second experiment was carried out as follows:

Solutions were made up each containing exactly 0.5 gram total solids per 100 cc. and the same procedure followed as in the first experiment. The amount absorbed was this time based on the total solids figure instead of the tannin, and resulted as follows:

TABLE II.

Material	Per cent. of matter absorbed based on the total solids
Galls	21.3
Sumac	17.2
Myrobalans	16.6
Divi-divi	16.0
Quebracho	19.7

The above figures are no doubt only approximate, for it is possible by various methods of extraction to vary the character of extract obtained and consequent variation in the amount absorbable by cotton, so that in order to obtain relative absorption values it will be necessary to carry out this method on each individual extract.

To obtain the relative mordanting values of the various tanning materials, the cotton used in the above experiments was washed and passed through an iron bath, ashed, and the amount of iron fixed, determined. For the first experiment, each part of matter absorbed fixed the following percentage of iron, calculated in the table as Fe_2O_3:

TABLE III.

Material	Combining percentage
Galls	36.5
Sumac	33.5
Myrobalans	34.5
Divi-divi	32.4
Quebracho	24.4

In order to obtain a relative mordant value, the two figures representing the absorption and combining value were multiplied together and resulted as follows on a tannin percentage base:

TABLE IV.

Material	Mordant value according to tannin content
Galls	92
Sumac	91
Myrobalans	77
Divi-divi	59
Quebracho	42

The above figures are of course simply relative and arbitrary.

This so-called mordant value should agree with the depth of color obtained on cotton, but failed on this test to correspond, the sumac showing the greatest depth, followed by galls, myrobalans, divi-divi, and quebracho in order. In explanation of this non-agreement, it is only fair to state that this is no doubt due to the natural coloring matters referred to above, all the materials with the exception of galls producing marked colorations on the cotton before passing through the iron bath.

A duplicate of the above was run on the cotton from the second experiment and resulted as follows:

TABLE V.

Material	Combining percentage
Galls	63.6
Sumac	68.6
Myrobalans	58.8
Divi-divi	50.0
Quebracho	33.4

Again multiplying the absorption value and combining value together we find the mordant value, according to total solids content, to run as follows:

TABLE VI.

Material	Mordant value according to total solids content
Galls	135
Sumac	118
Myrobalans	98
Divi-divi	80
Quebracho	66

The actual color depths on cotton agreed in relative value with these figures, but an attempt at verifying them on an actual percentage base failed owing to the fact that the various shades produced by the different tanning materials made it impossible to effect exact color matches.

It should be noted also that while galls, sumac, myrobalans, and divi-divi belong to the "iron-blue" tannins, quebracho is an "iron-green" one and any attempt to match shades on such a base will result in inevitable failure. Going further into the chemistry of the tannins, we find that there is probably little

doubt that the principal if not the only tannin of galls and sumac is gallotannic acid, sumac also containing more or less of a coloring matter called myricetin. Myrobalans and divi-divi also contain large amounts of ellagitannic acid which may or may not be allied with the coloring matters. In any case, the actual iron-mordanting value of any tanning material seems to rest on the amount of true gallotannic acid present, which fact is borne out in Table VI, and until some method of tannin analysis is devised which will return this reading only, it will be necessary to follow some such method as outlined above in order to determine these values. This is not said to detract from the present Official Method of tannin analysis for it is no doubt correct for the purpose for which it is used, inasmuch as it is generally accepted in the leather and tanning industries that all matters absorbable by hide from vegetable tanning materials which are capable of converting animal skin into the imputrescible material known as leather may legitimately be termed tannin.

In conclusion, it may be stated that in general it is possible to approximate roughly the comparative mordant value of any of the above tanning materials if a tannin analysis of said material is available. With the possible exception of galls, the price of all these tanning materials is based on their tannin content as returned by the Official Method and an analysis is generally submitted. By multiplying the total solids figure by the mordant value as shown in Table VI, comparative values will at once be shown. Of course these figures apply only to extracts of known purity. In particular cases and where the purity of the extract is unknown, it is desirable to carry out the prescribed method.

In general, however, on pure extracts, the mordant values as shown in Table VI should be approximated, and expressed in percentages, using galls as a base, are as follows:

	Per cent.
Galls	100.0
Sumac	87.4
Myrobalans	72.6
Divi-divi	59.3

As quebracho is an "iron-green" tannin and really not comparable with the others as a mordant, it is perhaps best to exclude this from the above table. Quebracho is, however, a valuable weight-giver as illustrated in Table II and is in fact used considerably in various branches of the textile industry.

THE ACTION OF NEUTRAL CHLORIDES UPON CHROMIC CHLORIDE SOLUTIONS.

By Mabel E. Baldwin, M. A.

In earlier work[1] upon the action of neutral salts upon chrome liquors, chromic sulphate solutions were employed, but it was found that the addition of chloride salts caused an increase in acidity, as determined by the electrometric method, whereas the addition of sulphates caused a decrease followed by an increase with higher concentrations of added salt. This difference in the action of sulphates and chlorides rendered it advisable to perform series of experiments in which there should be no chance for chemical reaction between the chrome compound and the added salt other than the direct formation of addition compounds. For this reason the present work has been confined to the simpler action of chloride salts upon chromic chloride solutions and the result has been a decided advance toward a more complete explanation of the so-called "Neutral Salt Effect" in chrome tanning. Some further work is now under way on the more involved action of sulphates upon chromic sulphate solutions, after which it is purposed to begin work on the chrome tanning process itself.

The neutral salt effect is one of the several factors involved in the mechanism of chrome tanning. That chrome tanning is an extremely complicated process is unquestionable and it is only after each one of its component reactions and the underlying principles are understood that the tanning process can be efficiently controlled. The rôle of neutral salts in chrome tanning is therefore a subject of great interest and importance.

In the process of tanning it has been observed that the addition of sodium chloride makes possible the use of more basic chrome liquors. The same liquors without sodium chloride yield precipitates of basic chrome salts. Sodium chloride, therefore, appears to have the power of stabilizing the solution, or of retarding or preventing precipitation. In a recent investigation of this property of salt, Wilson and Kern[2] found that if chrome liquors are identical in composition except for a difference in the neutral

[1] This paper is a continuation of a study of the chemistry of chrome tanning begun in 1917 by Thomas and Baldwin. This JOURNAL, 13, 192, 248 (1918).

[2] This JOURNAL, 12, 445 (1917).

salt content, the one containing the largest amount of salt requires the greatest quantity of alkali to start precipitation, although the total amount of acid hydrogen in each is the same. From a comparison of the influences of different kinds and amounts of neutral salts upon the quantity of alkali required to start precipitation with the degree of hydration of the same salts at infinite dilution, they concluded that the neutral salt effect was due to the formation of hydrates in solution. It appeared from their results that the addition of neutral salts has the effect of increasing the actual concentration of hydrogen ion in the solutions. Electrometric measurements carried out in this laboratory show that in the case of neutral chlorides this is true. The results are in perfect agreement with the explanation of the neutral salt effect advanced by Wilson and Kern.

In order to measure the concentration of hydrogen ion present in chromium chloride solutions containing varying kinds and quantities of neutral chlorides, the following experiments were performed. A concentrated solution of chromium chloride was made by dissolving the pure salt in water and filtering. By adding to increasing amounts of several different neutral salts equal quantities of this solution, and water to a definite volume, a series of solutions was prepared in which the resulting concentration of chromic oxide was 13.77 grams per liter and the concentrations of the salts 0, 1, 2, 3, and 4 molar. The salts used were the chlorides of sodium, potassium, ammonium, lithium, and barium. The concentration of chromic oxide was determined by the Provisional Method of the A. L. C. A. Immediately after preparing each solution the concentration of hydrogen ion was determined and the determinations were repeated after the solutions had stood for 50 days.

The results are given in Table I and Fig. 1. They show that the hydrogen ion concentration in these solutions, in the composition of which the concentration of neutral salt is the only variable, is increased by the presence of the neutral chloride, and the greater the amount of salt the greater the concentration of hydrogen ion, although the total amount of acid hydrogen remains the same. Moreover, the salts differ among themselves in their power to increase the hydrogen ion concentration. When the salts are

TABLE I.—Effect of Neutral Chlorides upon the Concentration of Hydrogen Ion of Chromium Chloride Solution.

Conc. salt	Log. CH+ (Immediately)	Conc. hydrogen ion moles per liter (Immediately)	Log. CH+ (After 50 days)	Conc. hydrogen ion moles per liter (After 50 days)
Sodium Chloride.				
0	—2.22	0.00603	—2.40	0.00398
M	—2.06	0.00871	—2.24	0.00575
2M	—1.91	0.01330	—2.11	0.00776
3M	—1.75	0.01778	—1.95	0.01122
4M	—1.59	0.02570	—1.79	0.01622
Potassium Chloride.				
0	—2.22	0.00603	—2.40	0.00398
M	—2.15	0.00708	—2.36	0.00437
2M	—2.06	0.00871	—2.28	0.00525
3M	—1.97	0.01072	—2.19	0.00646
4M	—1.88	0.01319	—2.12	0.00759
Ammonium Chloride.				
0	—2.22	0.00603	—2.40	0.00398
M	—2.14	0.00724	—2.36	0.00437
2M	—2.07	0.00851	—2.30	0.00501
3M	—1.97	0.01072	—2.19	0.00646
4M	—1.88	0.01319	—2.14	0.00724
Lithium Chloride.				
0	—2.22	0.00603	—2.40	0.00398
M	—2.01	0.00977	—2.22	0.00603
2M	—1.82	0.01514	—2.04	0.00912
3M	—1.62	0.02398	—1.80	0.01585
4M	—1.41	0.03891	—1.60	0.02510
Barium Chloride.				
0	—2.22	0.00603	—2.40	0.00398
M/4	—2.09	0.00813	—2.32	0.00479
M/2	—2.02	0.00955	—2.23	0.00589
3M/4	—1.93	0.01175	—2.13	0.00741
M	—1.86	0.01380	—2.05	0.00891

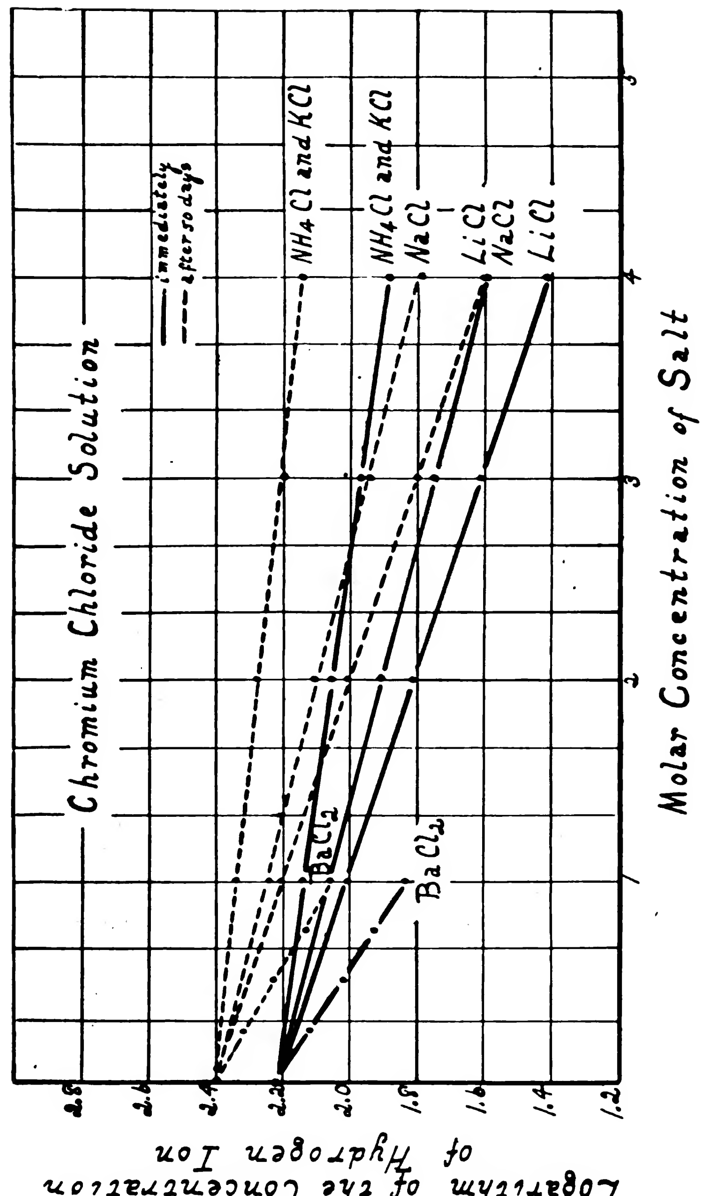


FIG. 1.
The logarithmic values are negative.

arranged in order of their ability to increase the actual acidity, we get the following series:

$$\begin{matrix} KCl, \\ NH_4Cl, \end{matrix} NaCl, LiCl, BaCl_2.$$

In order to learn whether the hydrolysis of the chromium salt was a factor in influencing these results, similar series of experiments were carried out using 0.1 molar and 0.004 molar hydrochloric acid in place of chromium chloride. Hydrochloric acid of concentration equal to 0.004 molar was chosen so that the concentrations of hydrogen ion should be approximately the same as in the chromium chloride solution.

When the chlorides that were used in these experiments are placed in order of their increasing degree of hydration at infinite dilution, we get the series:

$$KCl, NH_4Cl, NaCl, LiCl, BaCl_2.$$

In this series the salts occupy the same relative positions as in the neutral salt effect series given above, except for KCl and NH_4Cl, which is because these two salts are quantitatively very nearly alike, as is seen from the number of molecules of water combined with the ions of the salts at infinite dilution:[3]

K^+, 9.6; NH_4^+, 10.7; Na^+, 16.9; Li^+, 24.0; Ba^{++}, relatively higher.[4]

The salt which unites with the greatest number of molecules of water is the salt which is most effective in increasing the hydrogen ion concentration, and therefore in increasing the amount of alkali necessary to start precipitation in a chrome liquor.

A comparison of the results of the acid series given in Tables II and III and Figs. 2 and 3 with those of the chromium chloride series in Table I and Fig. 1 shows that the neutral salt effect is not a result of the hydrolysis of the chromium salt. As is easily seen from the curves, the change in hydrogen ion concentration, due to the presence of the neutral chlorides, in the chromium chloride solution is of the same order and approximately the same magnitude as that in the hydrochloric acid solutions of

[3] G. M. Smith, *J. A. C. S.*, **37**, 722 (1915).

[4] E. W. Washburn, *Tech. Quart.*, **21**, 360 (1908).

comparable dilution. But the change that has taken place in the actual acidity of the chromium chloride series after long standing is similar in each solution and apparently independent of the kind and amount of chloride present.

TABLE II.—EFFECT OF NEUTRAL CHLORIDES UPON THE CONCENTRATION OF HYDROGEN ION OF HYDROCHLORIC ACID, 0.1 N.*

Conc. salt	Log. CH+	Conc. hydrogen ion moles per liter
	Sodium Chloride.	
0	—1.04	0.09120
M	—0.88	0.13183
2M	—0.72	0.19053
3M	—0.52	0.28185
4M	—0.36	0.43650
	Potassium Chloride.	
0	—1.04	0.09120
M	—0.95	0.11220
2M	—0.85	0.14126
3M	—0.75	0.17780
4M	—0.63	0.23445
	Ammonium Chloride.	
0	—1.04	0.09120
M	—0.94	0.11482
2M	—0.87	0.13486
3M	—0.75	0.17780
4M	—0.65	0.23400
	Lithium Chloride.	
0	—1.04	0.09120
M	—0.81	0.15490
2M	—0.60	0.25120
3M	—0.35	0.44670
4M	—0.12	0.75870
	Barium Chloride.	
0	—1.04	0.09120
M/4	—0.96	0.10962
M/2	—0.88	0.13183
3M/4	—0.80	0.15883
M	—0.71	0.19500

* Compare results of H. S. Harned, *J. A. C. S.*, 37, 2460 (1915).

TABLE III.—Effect of Neutral Chlorides upon the Concentration of Hydrogen Ion of Hydrochloric Acid, 0.004 N.

Conc. salt	Log. C_{H+}	Conc. hydrogen ion moles per liter
Sodium Chloride.		
0	—2.49	0.00324
M	—2.27	0.00537
2M	—2.10	0.00794
3M	—1.88	0.01319
4M	—1.69	0.02042
Potassium Chloride.		
0	—2.49	0.00324
M	—2.39	0.00407
2M	—2.28	0.00525
3M	—2.17	0.00676
4M	—2.03	0.00933
Ammonium Chloride.		
0	—2.49	0.00324
M	—2.37	0.00427
2M	—2.27	0.00537
3M	—2.18	0.00661
4M	—2.03	0.00933
Lithium Chloride.		
0	—2.49	0.00324
M	—2.21	0.00617
2M	—1.95	0.01122
3M	—1.67	0.02138
4M	—1.40	0.03981
Barium Chloride.		
0	—2.49	0.00323
M/4	—2.40	0.00398
M/2	—2.30	0.00501
3M/4	—2.20	0.00631
M	—2.10	0.00794

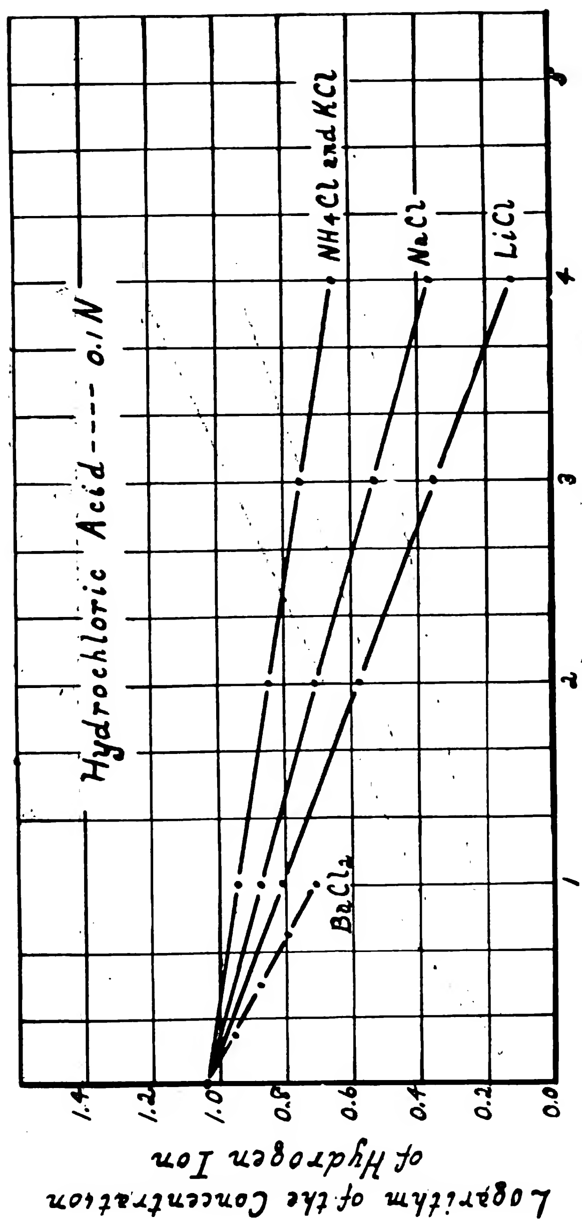

Hydrochloric Acid ---- 0.1 N
NH4Cl and KCl
NaCl
LiCl
BaCl2
Molar Concentration of Salt
1
2
3
4
5
Logarithm of the Concentration
of Hydrogen Ion
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0

FIG. 2.

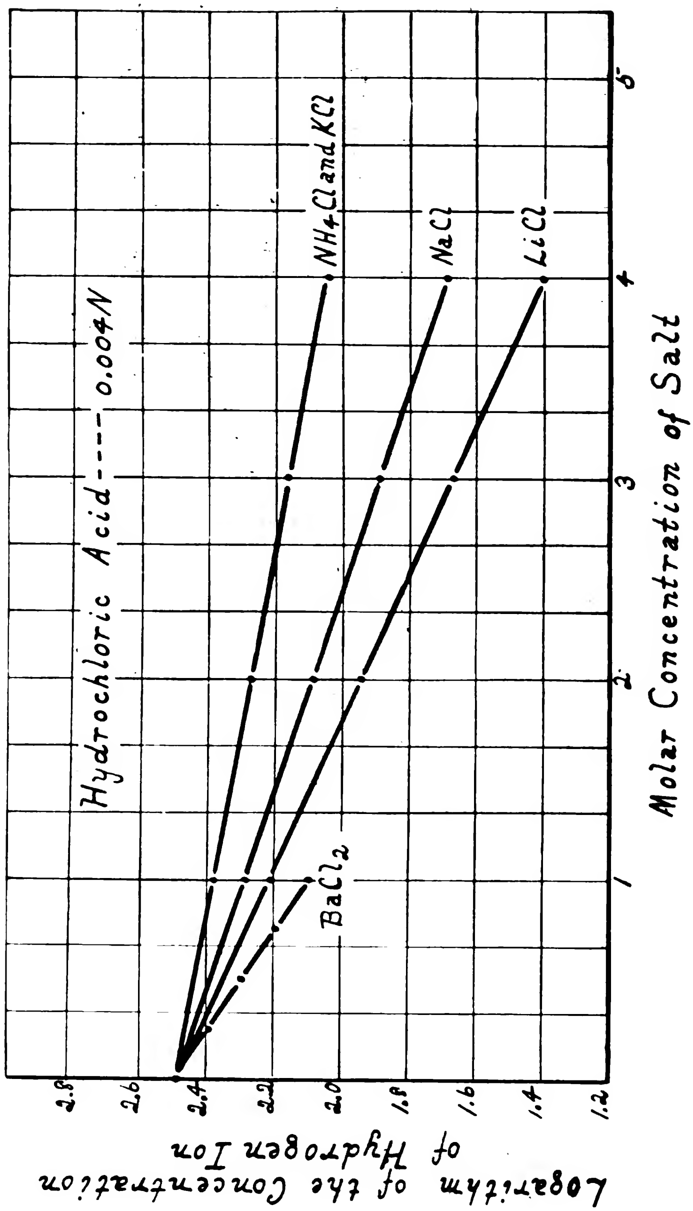

Hydrochloric Acid---- 0.004N
NH_4Cl and KCl
NaCl
LiCl
$BaCl_2$
Molar Concentration of Salt
1
2
3
4
5
Logarithm of the Concentration of Hydrogen Ion
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2

FIG. 3.

According to the theory which has been offered by Wilson and Kern as an explanation of the neutral salt effect, "it is necessary to distinguish between quantity of acid per liter of solution and quantity of acid per liter of solvent." In aqueous solution the molecules and ions of a salt combine with molecules of water. Since these hydrated particles, each one of which contains a comparatively large number of molecules of water, function as the units constituting the solute, a portion of water is removed from the solvent, and the amount of water acting as solvent is thereby diminished. This has the effect of increasing the hydrogen ion concentration. Actual acidity, as differentiated from total acid hydrogen, appears therefore to be due not to the concentration of hydrogen ion in moles per liter of solution, but to a ratio between the number of hydrogen ions and the number of water molecules.

That the hydrate theory affords an explanation of the neutral salt effect is thus made much more vivid by electrometric measurements of hydrogen ion concentrations.

Continued study[5] of the chemistry of chrome tanning is expected to explain other factors in the mechanism of the reaction and to make chemical control of the industry much more scientific and profitable.

We are greatly indebted to A. F. Gallun & Sons Company of Milwaukee for their generous support of this research and to Mr. John Arthur Wilson for his valuable suggestions in planning the experiments and in interpreting the results during the absence of Dr. Thomas.

[5] **Owing to the fact that Dr. Thomas has been in France during the past year, this work has progressed slowly compared with his original plans, but we may now expect his early return.**

LABORATORY OF COLLOID CHEMISTRY,
Havemeyer Hall, Columbia University,
New York City, December, 1918.

DEGREE OF TANNAGE IN DIFFERENT STAGES OF PROCESS.

By Oskar Riethof.

[The following paper was received before the publication of Dr. Rogers' work, "The Absorption of Tannic Acid in Sole Leather Manufacture" (this JOURNAL, November, 1918). Mr. Riethof has requested the editor to say that he was not referring to Dr. Rogers' paper, but to his remarks made at the last A. L. C. A. meeting.—EDITOR.]

At the last meeting of the American Leather Chemists Association, during a discussion on problems for the consideration of the American Research Laboratory,[1] Dr. Allen Rogers made the remark that it should be one of the problems for the research chemist to study the degree of tanning in different stages of the process. In making their inventories most tanners assume that the stock in process on the average is half tanned. In work done on this line Dr. Rogers found that this is erroneous; that, in fact, when the hides, after about 40 days, are coming from the second layer, they are four-fifths tanned, and the other 60 days are required for completion of the tannage. This fact is important because the difference means a considerable amount of money.

It is a coincidence that the writer made during the last year a number of sets of experiments along the same lines and here will give an extract of the results obtained in order to avoid duplication of work by other chemists.

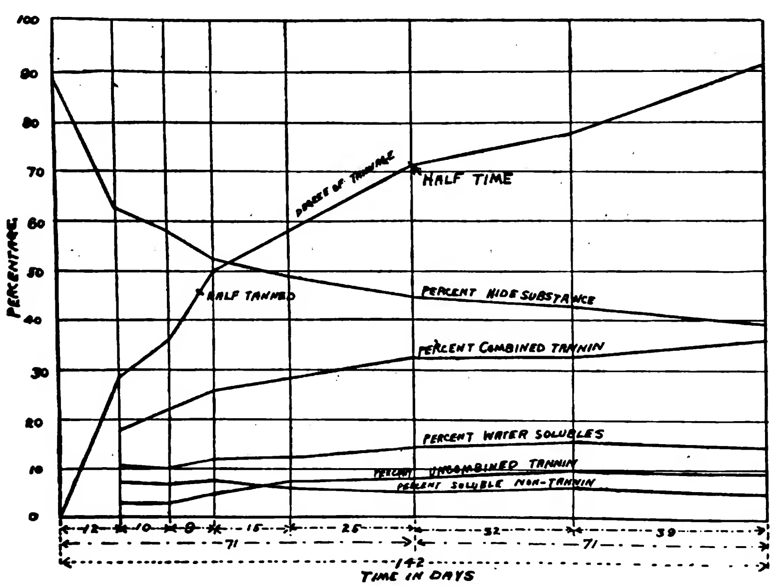
Dr. Gordon Parker in a paper entitled "The Application of Kjeldahl's Method of Estimation of Nitrogen in the Tan-yard as a Means of Controlling the Tanning and Finishing of Sole Leather,"[2] published three tables showing the progress of the tanning process for three individual English tannages. All results are figured on basis of 14 per cent. moisture. Parker adds the figures for moisture, mineral ash and hide substance and calls the difference between these figures and 100, *tannin*. He used this figure in a column which he calls "Tannin absorbed by 100 parts of hide substance." But his tannin figure includes besides the combined tannin all water solubles and therefore non-tannin. For this reason his tables do not give us any information as to

[1] This JOURNAL, August, 1918, p. 398.

[2] *J. S. C. I.*, June 30, 1902; *Collegium*, 1902, p. 236.

the "degree of tannage" which figure tells us, according to Schroeder, the parts tannin actually combined with 100 parts hide substance.

The samples used by the writer in the experiments were cut along the backbone in the usual way, 24 inches from the root of the tail, the sediments on the grain and flesh side removed as much as possible and the dried pieces subjected to a complete analysis according to the methods of the A. L. C. A. The results of one set of tests are given in the chart. All figures are based on 10 per cent. moisture. The degree of tannage from the sixth layer is 90.3; half of the tannage was completed in 27 days and half time (71 days), the figure for the degree of tannage was 71.3, or in other words, in half time the leather was four-fifths tanned.



Two other sets of tests carried on in different yards gave the following results:

1st Set: Degree of tannage from sixth layer after 108 days, 84.8; the stock was half tanned in 24 days, somewhere in the second layers; in half time the degree of tannage was 64.0, or in

other words, the stock in half time was about three-fourths tanned.

2nd Set: Degree of tannage from fifth layer after 87 days, 86.2; the stock was half tanned in 29 days, when coming from second layer; in half time the degree of tannage was 64.3, or, as above, the stock was three-fourths tanned.

It would be impossible to give a fixed rule for the extent of the tannage in half time, because this depends on many factors, as yard schedule, strength of liquors, their composition, weight of stock, etc., but as a rule for our standard sole and belting leather tannages, we can safely say, in half time the stock is between three-fourths to four-fifths tanned which is in accordance with Dr. Rogers' results.

The writer agrees with Dr. Rogers that this discrepancy means a considerable sum of money, especially for big concerns. A set rule as to what this difference amounts to for a yard of given size cannot be given, because this is influenced to a certain extent by conditions as outlined above and in addition by the price per tan unit of the tanning materials employed, but we will not be far off when we give the difference as about $500 for every 1,000 pounds hide weight soaked in per day. This covers the value of tanning which is taken up by the hide in excess of the credit given to the yard stock when figured on the average as half tanned.

CORRECTION.

On page 536, November, 1918, the heading of the second column in the table should read "Still soluble after" and not "Rendered soluble after."

ABSTRACTS.

Hydrolysis of Fish Gelatine. *Les Matières Grasses,* Sept. 15, 1918, p. 4977. In order to ascertain whether fish gelatine differs in chemical composition from ordinary bone gelatine, Y. Okuda has hydrolyzed the product derived from shark skin with HCl, with BaO, and with H_2SO_4, and has studied the resulting products. The total nitrogen and its distribution are practically the same in both cases, but fish gelatine yields rather more monoamino acids, and very much more glycocoll, alanine,

leucine, phenylalanine, glutamic acid, and aspartic acid than bone gelatine. The proline and serine contents of fish gelatine obtained by the ether method are so small as to be attributable to experimental error. The diamino acids exist in perceptible quantities in both gelatines.

J. A. W.

One of the Causes of Brittle Grain. A TANNER. *La Halle aux Cuirs,* Oct. 27, 1918; cf. this JOURNAL, 13, 401 (1918). Brittle grain is generally supposed to be due to poor beamhouse work and to the presence of lime, but it may often be due to poorly conducted drying. The writer found that he could cut a piece of leather in two and cause one piece to remain soft after drying and the other to become brittle, simply by varying the method of drying. Too rapid drying, either because of excessive heating or too much ventilation, produces brittle grain and this can, therefore, be prevented by proper control. The trouble is particularly noticeable in the case of rapid, vegetable tannages and in mineral tannages where much uncombined solid matter remains in the leather. If leather tanned with alum and salt be dried rapidly, the grain becomes wrinkled and spangled with fine white crystals of these salts, which does not happen in normal drying. In rapid drying the water in the interior of the leather is carried rapidly to the surface, and with it the soluble matter, while in slow drying the water does not flow, but evaporates, leaving the soluble matter distributed evenly throughout the body of the leather and preventing such an accumulation of these solids on the grain as to cause brittleness. The same is true for vegetable tannages where too rapid drying will cause a great concentration of uncombined tannins on the surface, which will result in brittle grain. Naturally in rapid tannages, where the proportion of uncombined tannins is very large, the danger will be correspondingly greater. In order to avoid the danger mentioned, it is suggested that the grain be very lightly oiled before drying, but care should be exercised not to use too much oil. J. A. W.

The Use of Mineral Oils. A. TANNER. *La Halle aux Cuirs,* Sept. 29, 1918. Mineral oils have had nowhere nearly such extensive application in the leather industry as oils of animal and vegetable origin, although the writer is aware of the following uses. A very light coating of the grain of leather with petroleum oil before drying not only retards evaporation and hinders oxidation, thereby giving a better color, but it guards against moulds which form when damp leather is piled or during drying when conditions favor their growth. The addition of mineral oil to the fat-liquor for white and wax calf serves as a double preventive: it hinders the growth of moulds and prevents in a large measure oxidation of the fats in the body of the leather, which is injurious because of its burning or corroding the leather. Paraffine is used to stuff chrome leather and makes a soft, smooth, and brilliant grain.

Attention is called to a paper by Earp (cf. this JOUR., 5, 225, 1910) who states that vegetable tannins not soluble in water may be dissolved

in mineral oil which in turn becomes soluble in tannin solutions. The writer also refers to the recent paper by Meunier (cf. this JOUR., 13, 530, 1918) and hopes that the uses for mineral oil in the tannery may increase.

J. A. W.

Progress of the Tanning Trade. CHARLES E. PARKER. *Leather Trades Review,* Nov. 13 and 27, 1918. In a lecture delivered at Leathersellers' College, Mr. Parker has sketched the progress of tanning in England during the last forty years. When he started tanning in 1878, tanneries were small, the work was done entirely by hand, wages were low, and the tanning materials, oak bark and valonia, were poorly ground and poorly leached. Since that time many new tanning materials, such as hemlock, chestnut and quebracho extracts, have been introduced. Although wages have greatly increased, the introduction of extract, together with other saving devices, has cut the cost of tanning from 5d. per pound of leather in 1878 to 1½d. in 1913.

New machinery has been continuously introduced, the very latest being a mechanical liming proposition, all of which save both time and labor, and improve the appearance, the gain and the quality of the leather. He deals lightly with the development of chrome tanning with which he has not had much experience. He, however, lays great stress on the importance of chemistry to the tanning industry. Great credit is given to H. R. Procter and Dr. Gordon Parker for their work as instructors in this line. Mr. H. R. Procter was one of the first leather chemists and for the last forty years has stood at the head of the world's science of leather manufacture. Mr. Parker lays stress on the chemist having received special training in leather chemistry. War conditions have brought the tanning chemist to the front and he has become almost indispensable to the English tanning industry.

The World's Trade in Hides, Skins and Leather. *S. and L. Reporter,* Nov. 28, 1918. This is an article prepared for the Tanners' Council by E. A. Brand, General Secretary, and gives in great detail, with many tabulations, the world's dealings in hides and skins, both tanned and untanned.

Adsorption by Hide Powder. V. KUBELKA. *Kolloid. Zeits.,* 1918, 23, 57-68; reprinted from *J. S. C. I.* As a result of experiments on the removal of hydrogen chloride from aqueous solution by hide powder, it has been found that the hide substance retains its absorbing capacity unchanged for at least two years when the powder is preserved in a carefully stoppered bottle. The equilibrium between the hide powder and the acid solution is rapidly attained and in the case of pure hydrochloric acid solutions the quantity of acid in the hide is independent of the concentration of the acid in the aqueous solution. For acids of concentration N/100 to N/1, the quantity of hydrogen chloride fixed by 1 gram of dry hide powder is found to be 0.739 millimol. In presence of considerable quantities of sodium chloride, hydrogen chloride is removed

more easily from the aqueous solution and under these conditions the amount of acid in the hide powder depends on the concentration. From solutions saturated with respect to sodium chloride, the quantity of hydrogen chloride absorbed by 1 gram of hide powder increases from 0.773 millimol. in the case of 0.008 N acid to 1.655 millimol. in the case of 0.95 N acid. The graphic representation of the actual results suggests that the phenomenon is of complex character in that the absorption curve consists of two distinct branches. The first portion of the curve appears to reach a maximum corresponding with the absorption of 1 gram-mol. of HCl per 977 grams of hide powder and it is supposed that this indicates the formation of a definite compound between the hide substance and the acid. The number 977 would thus represent the molecular weight of the hide collagen. The second branch of the absorption curve is of the normal adsorption type and it is inferred that the compound formed is capable of removing further quantities of hydrogen chloride from aqueous solutions containing sodium chloride in virtue of its adsorptive faculty.

Researches on Lignin: Lignosulphonic Acids. M. Hönig and J. Spitzer. *Monatsh. Chem.*, 1918, 39, 1-14; reprinted from *J. S. C. I.* By the careful evaporation of sulphite-cellulose waste liquor it is possible to obtain a solution of "lignosulphonic acid" which by conversion into the calcium or barium salt and subsequent fractional precipitation from the aqueous solution by alcohol, can be separated into several fractions of different composition. The barium salt obtained in this way can be separated into fractions of the composition $C_{46}H_{50}O_{18}S_2Ba$, containing four methoxyl groups, $C_{40}H_{44}O_{18}S_2Ba$, containing one methoxyl group, and $C_{74}H_{114}O_{48}S_2Ba$, containing three methoxyl groups, the last formula referring to the portion which remains unprecipitated. The salts thus obtained are amorphous brown solids whilst the corresponding free acids are soluble in water, ethyl alcohol, or acetic acid and liberate carbon dioxide from carbonates.

Chrome Retanned Upper Leather. H. L. Nunn. *S. and L. Reporter*, Nov. 28, 1918. Mr. Nunn has just returned from Europe where he has been investigating the wear of army shoes. The English and the French have always contended that bark tanned leather was superior to the chrome retanned. After collecting a great deal of evidence, Mr. Nunn was called into a conference at Quartermaster Headquarters. By practical reasoning and by actual results proven by shoes worn in the field the superiority of chrome retanned leather was demonstrated. Chrome retanned leather has a stronger, tougher fiber, is softer and will stay softer longer with abuse than bark leather. Bark leather after getting wet, especially if not properly cared for, gets very hard and will burn easily if put near the fire while wet. The water resisting qualities do not depend on the kind of leather, but on the grease in the leather. Mr. Nunn said the English were gradually coming to the belief that chrome retanned leather was the better leather.

British Exhibit of Shoes and Leather Substitutes. *Commerce Reports.* An exhibition of footwear and leather substitutes was held in London in October. The majority of exhibits were made up of sole-leather substitutes and emphasize the progress that has been made in Great Britain in developing substitute materials in an industry which has had to devote a large share of its normal supply of sole leather to the requirements of the allied armies and navies. Twenty-six manufacturers of substitute soles were included in the list of exhibitors, which is more than three times as many as took part in the first exhibition of this character held last year.

While the progress which has been made in Great Britain in the matter of developing the substitute industry has not been so extensive as in the United States, it is undoubtedly true that there has really been a significant growth of interest in this subject among the British trade. One of the firms represented at the exhibition has just taken an order for 25 tons of its product for export to Australia; and although the domestic business in substitute soles has not yet developed to any considerable proportions, the possibilities of building up an export trade are already receiving considerable attention. It is stated that in July and August 200,000 pairs of boots were made with substitute soles in Great Britain, which is an indication of the extent to which leather substitutes are filling at least a temporary want in the British shoe industry.

Experiments with Tanning Stuffs in Madras. *Commerce Reports.* The following press communique has been issued by the Government of Madras in India:

The public are, perhaps, not aware that, in addition to the teaching work carried on at the leather trades school, Washermanpet, quite a number of interesting experiments are being carried on to ascertain the value of new tanstuffs and mixtures. The immense demands made by the war for tanned hides has brought into great prominence the question of supplies of tanning barks and of substitutes for the bark of the avaram shrub, which is, of course, the leading tanning material of southern India. A consignment of black wattle bark was imported last year from South Africa, and various experiments were tried, some with wattle bark alone and others with mixtures of wattle and avaram in different proportions. The bark of the twig and trunk of *Anogeissus latifolia* has also been experimented upon with promising results, as also have sumacs made from the powdered leaves of the tree. A number of other substitutes are being tried.

Precipitant for Sugars, Starches, Gums, Proteins, etc. W. SCHULTE. *Chem. Zeit.*, 1917, 822; *J. S. C. I.*, 1918, 101a. Ammoniacal lead acetate solution precipitates the following substances from aqueous solution: sucrose, invert sugar, dextrose, lactose, dextrins, and starch; gum arabic, gum tragacanth, albumin, casein, gelatin, pepsin and peptone; benzoic, salicylic, and picric acids, and phenol. Lead acetate alone precipitates

citric, tartaric, malic, tannic, gallic and succinic acids, and pyrogallol. The reagents must be freshly prepared as it rapidly absorbs atmospheric carbon dioxide, and is made by mixing 100 cc. saturated lead acetate solution with 26 cc. water and 8 cc. ammonia (specific gravity 0.91). This reagent indicates phenol or gum arabic at a concentration of 1 in 20,000, and sugars at 1 in 10,000. Precipitates may be collected, washed with dilute ammonia, dried at 100° C. and weighed. The application of a factor will give the weight of substance precipitated.

Sodium Sulphide in Lime Liquors. H. HAYES. *J. S. L. T. C.*, October, 1918. An excess of standard zinc sulphate solution is added to a known quantity of filtered lime liquor in a graduated flask; acetic acid added to distinct acidity and the flask filled to the mark. The mixture is shaken and filtered. To an aliquot part of the filtrate 2 or 3 cc. of strong hydrochloric acid, and 2 or 3 grains of ammonium chloride are added; the solution warmed to 40° C. and titrated by means of potassium ferrocyanide solution using uranium acetate as external indicator. The end point is quite distinct providing a minute or so is allowed to elapse after the addition of more reagent.

The following comparative values were obtained with a lime liquor using the ammoniacal zinc solution made according to the *Leather Chemists' Pocket Book* and the method described above:

Ammoniacal zinc method.....	1.65 grams Na_2S per liter
Excess zinc method..........	1.68 grams Na_2S per liter

In order to ascertain whether the presence of organic matter in the lime liquor affected the results, the amount of Na_2S in a simple sodium sulphide solution was estimated. The values obtained were:

Ammoniacal zinc method.....	4.68 grams Na_2S per liter
Excess zinc method..........	4.73 grams Na_2S per liter

Basicity of Chrome Liquors. H. R. PROCTER. *J. S. L. T. C.*, October, 1918. Procter suggests as more scientific, that the basicity of chrome liquors should be stated as the proportion of basic valencies to acid ones, the normal salt being unity. Thus $Cr_2(SO_4)_3$ would be $\frac{6}{6} = 1$. $CrCl_2OH$ or $Cr_2(SO_4)_2(OH)_2$ would be $\frac{3}{2} = 1.5$ and so on. Acid salts such as bisulphates would be 0.5. For chrome salts the simple rule would be that the weight of Cr_2O_3 found (in mgr.) should be divided by $\left(\frac{152}{6} \times \text{cc. N/1 alkali}\right.$ consumed in neutralizing the acid).

Determination of Nitrogen by Kjeldahl's Method. S. P. L. SÖRENSEN. *Comptes-Rendus des Travaux du Laboratoire de Carlsberg; J. S. L. T. C.*, Nov., 1918. The author after numerous experiments with the original

Kjeldahl method, the Gunning modification and the Gunning-Arnold method recommends the following method for the determination of protein nitrogen:

In a long-necked flask (250 cc.) made of Jena glass a measured or weighed quantity of the solution to be analyzed is heated over a good Argand burner, together with 20 cc. of concentrated sulphuric acid, 5 grams potassium sulphate, and a small piece of copper wire (about 50 milligrams). To begin with we heat gently until the water has evaporated; later on the temperature is raised so as to maintain the liquid at or near its boiling point. While repeatedly shaking—in order to bring down all carbonized particles into the liquid, that they may be completely decomposed—the liquid is heated till it has acquired a marked green color (2-4 hours), when the heating is continued for 5 hours more. The still boiling liquid is then oxidized by adding cautiously, three times, about 0.5 gram of dry, pulverized potassium permanganate, the flask being well shaken after each addition. After being completely cooled, the liquid is diluted with water, and the ammonia distilled off as usual.

Journal of the

American Leather Chemists Association

Vol. XIV FEBRUARY, 1919 No. 2

W. K. ALSOP . . . . Editor and Manager
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Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $6.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized July 16, 1918.

ELECTIONS.

ACTIVE.

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ASSOCIATE.

J. M. Roberts, Secretary, Central Scientific Co., 460 East Ohio St., Chicago, Ill.

CHANGE OF ADDRESS.

Frank M. Loveland, 151 Park St., Corry, Pa.

RECENT DEVELOPMENTS IN LEATHER CHEMISTRY.*

By Henry R. Procter, D.Sc., F.I.C.,

Emeritus Professor of the Chemistry of Leather Manufacture, Leeds University; Director of the Procter International Research Laboratory.

LECTURE II.—DELIVERED MAY 14TH, 1918.

We are now in a position to consider the actual changes of the tanning process, which are partly chemical and partly dependent on the physical process known as "adsorption," which itself may often be merely a surface chemical reaction which cannot be completed in limited time.

So far we have discussed the processes necessary for the preparation of the hide or skin for tanning. It now remains to study its actual conversion into leather. Up to this point, though cleansed and free from extraneous appendages, the hide remains merely raw pelt, wet and easily putrescible, or, if dried, hard, horny, and translucent. Leather, on the other hand, is non-putrescible, opaque, and pliable, when dry, to a greater or less degree.

It is now sixty-five years since Knapp, in a remarkable thesis on "The Nature and Essence of Tanning," gave the first intelligible account of the nature of the change. As has been stated, the raw hide consists of a mass of fibres swollen with water, existing partly in the jelly of which the fibres consist, and partly retained by capillarity between them. If allowed to dry, the loosely-held capillary water evaporates, and the jelly-fibres come into contact while still moist and swollen, and adhere to a solid mass. If on the other hand the fibres can be made to give up the jelly-water while still separated, they no longer adhere, but remain as a fibrous felt with all the physical characteristics of leather. Knapp accomplished this by soaking the pelt in alcohol, in which the fibres are not soluble, and which gradually took the place of the capillary water, and then removed that of the jelly, so that on finally evaporating the alcohol no adhesion took place. Such a leather, if soaked in water, slowly returned to the raw-hide condition, but if a little stearic acid was dissolved in the alcohol it remained as a coating on the fibres and prevented

* *J. R. S. A.*, Nov. 8, 1918. (See this JOURNAL, 12, p. 582, 1918.)

or delayed their re-absorption of water. On these facts he based the theory that the essential of tanning was the coating of the fibres with some constituent of the tanning solution which would make them non-adherent, and he concluded that tanning was a mechanical rather than a chemical process.

Knapp's conclusions were only a part of the truth. He offered no explanation of the causes of dehydration, which, in my view, is an essential part of the operation; and he could not know of the production of permanent leathers by formaldehyde and by bromine, from which no coating substances can be deposited, but which alter the chemical nature of the fibre itself.

Let us first take the tawing or ordinary alum and salt tannage, and consider how far we can apply to it the principles we have already discussed. Aluminium sulphate (which is now generally substituted for alum) partially hydrolyzes on solution into sulphuric acid (hence its sour taste) and alumina which remains in solution (possibly colloidal), with an excess of the normal salt. If hide be placed in such a solution it absorbs the free sulphuric acid and swells, and as free acid is essential to prevent hydrolysis a further portion of acid is liberated and absorbed, and the hydrolysis proceeds much further than it would in absence of the hide, leaving an alumina solution in which the alumina base preponderates over the acid, and which is possibly to be viewed merely as a solution of alumina in the normal salt. Such solutions are known as basic. The swollen leather, if dried in this state, would prove stiff and undertanned, as swollen leather usually is. If, however, common salt be added to the mixture, pickling takes place, the swelling is reduced, and the fibres contracted, so that they dry without adhesion and a sort of leather is formed. These dehydrated and separated fibres now absorb or attract to their very extended surfaces the alumina from the basic solution in which it is very unstably dissolved, which increases the permanence of the non-adhesion. At first this deposition is probably purely mechanical, but if the leather is kept for some weeks under ordinary atmospheric conditions a further change takes place, possibly, as Wilson thinks, a chemical combination to a gelatine-alumina salt, from which the alumina can no longer be completely washed out. If in place of a normal aluminium sulphate solution one is used which has already been

rendered basic by the careful addition of soda, the hide does not swell, and the use of salt can be dispensed with, and a somewhat more permanent and more completely-tanned leather results.

Alumed leather is never very resistant to wetting, and chrome leather, which has largely replaced it, is very different in this respect, and if properly tanned will stand even boiling in water without shrinkage, and will remain soft on drying. It was first made by Professor Knapp in 1852, but he, unfortunately, did not perceive its value, and it was left to be re-invented in America by Augustus Schultz in 1884, who produced it by a different method.

Chromium exists in its salts in several different degrees of oxidation, and those of tri-valent chrome are of precisely the same type as those of alumina, and hydrolyze and form basic solutions in a similar way. Chrome alums are the counterparts of alumina alums, in which chrome oxide (Cr_2O_3) is substituted for alumina (Al_2O_3) and in principle basic chrome tannage is identical with alumina tannage, though it yields a much more perfect sort of leather. Chrome alum with sufficient salt will produce a lightly-tanned but very pliable leather, but in practice basic solutions are always used, salts of the empirical formula, $Cr\begin{cases}Cl_2\\OH\end{cases}$, or the corresponding sulphates being generally suitable, though for special reasons more or less basic solutions are often employed. Chrome salts are manufactured from chrome iron-ore, by furnacing with potash or soda, or with mixtures of these and lime, which yields a series of crystallizable yellow chromates, in which chromium trioxide acts as acid, precisely in the same way and with the same type of formula as sulphur trioxide in the sulphates and sulphuric acid. So also as SO_3 forms bi-sulphates with half the amount of base, CrO_3 forms bichromates, and these are the forms in which it occurs most abundantly in commerce. Bichromates readily give up three atoms of their oxygen, and hence are largely used as oxidizing agents in dye-manufacture and similar industries, and the reduced chromate yields crystallized chrome-alum which is thus often something of a by-product.

Hence for tanning purposes it is convenient, according to the

market, sometimes to start with chrome-alum, sometimes with bichromate, according to which is cheaper. In the case of chrome-alum all that is needed is to dissolve it in water, and then add gradually, and with constant stirring, a solution of ordinary washing soda, 25 to 30 per cent. of the chrome-alum used. Gradual mixture is essential, or the Cr_2O_3 precipitates, and will not redissolve. I published this process in 1898, and it has been largely used, but another formula I gave a year earlier, starting from bichromate, has also been very successful. In the latter the bichromate is dissolved in warm water, a quantity of sulphuric or hydrochloric acid, calculated to leave the desired basicity, is added, and then sugar or glucose. A violent oxidation sets in—some heat, and large quantities of CO_2 are produced, and the orange-yellow solution rapidly changes to a dark blue-green tanning liquor. Some aldehydes are also formed, which take part in the tanning, and yield a slightly softer leather than the chrome-alum liquor. A curious circumstance noted in this connection is that under some conditions a liquor results which is purplish instead of blue-green, and will not tan properly. A further investigation has revealed that this was due to the formation of saccharic or some other dihydroxy acid, and to the further discovery that the salts of dihydroxy acids, and especially Rochelle salt (sodium-potassium tartrate), have the power of completely redissolving the chrome from chrome leather, and again reducing it to the state of raw pelt, a fact not without its technical uses.

At the present time both chrome-alum and every form of glucose or sugar are scarce and costly, and it becomes desirable to devise some other mode of preparing chrome-tanning liquors. I find that if sulphurous acid gas, either pure or mixed with air, as from burning sulphur, is passed into a solution of bichromate till it smells of burning sulphur, a tanning liquor, or "chrome extract," is produced of suitable basicity for sole-leather, and which merely requires dilution. I publish this method now for the first time. A solution of sodium bi-chromate of 4 lb. per gallon of water gives an "extract" of about 18½ per cent. of Cr_2O_3. The equation is—

$$Na_2Cr_2O_7 + 3SO_2 + OH_2 = Na_2SO_4 + 2Cr(OH)SO_4$$

if the reaction is complete.

The tannage with such liquors can be done either by suspension in pits of liquors of gradually-increasing strength in about three or four days, or in rotating drums like churns, in a much shorter time and without difficulty.

I mentioned earlier that Schultz, in 1884, invented a different chrome-tanning process, and its principles will now be easily understood.* It is generally known as the "two-bath" process in distinction from the single-bath method just described. The prepared skins are first treated in an acidified bath of bichromate (practically one of dilute chromic or dichromic acid). This has no tanning effect, but the skins take up the free acid, and are colored bright yellow throughout. Only the free acid is absorbed, and a good deal of bichromate is often left in the bath, and sometimes thrown away.

The skins are now transferred to a reducing bath, generally of acidified sodium thiosulphate ("hypo"), containing free thiosulphuric acid and sulphurous acid, and it is here that the actual tannage takes place, the dichromic acid being reduced in and among the fibres to a tanning basic salt. The reducing process is chemically a very complex one, varying with the amount of acid used, and the rapidity of its addition, and even affected, as Stiasny has shown, by the trace of arsenic sometimes present in sulphuric acid; but free sulphur is regularly one of the products, and this, deposited between the fibres, tends to produce fulness and softness of the leather, which is usually also of a lighter color. In spite of its more complicated character, the two-bath method is quite as rapid as the one-bath, since the materials employed are all crystalloids, and diffuse into the skin more rapidly than the partially colloid one-bath liquors.

The hides or skins, having been converted into leather by either of the processes described, still contain free acid and chrome-salts not sufficiently basic to be permanently fixed. This is

[1] In his original process Schultz added only about two-thirds of the hydrochloric acid necessary for the complete liberation of the chromic acid of the bichromates, and, for some reason incompletely understood, the best results are not obtained when the exact theoretical quantity is used. Eitner has, however, got good results by using acid somewhat in excess of the theoretical amount (equal parts of bichromate and 33 ounces hydrochloric acid), and such a bath can be exhausted by a second lot of skins. Skins are also frequently pickled before chroming.

remedied by "neutralization," which consists in treating the skins with a weakly alkaline solution, so as to bring all the chrome present into a sufficiently basic state. If, however, *all* acid is removed from the chrome-salt, so as to leave Cr_2O_3 only, it appears to lose its tanning effect, and the skin becomes hard and pelty, so that considerable caution, and the use of alkaline solutions sufficiently weak completely to penetrate the skin without overhardening the surface, are essential. Weak solutions of borax are frequently employed, but even these have a hardening effect if used too freely, and a solution, proposed by Stiasny, of about 2 per cent. of ammonium chloride or sulphate and 2 to 4 per cent. of washing soda, is much better, as it can be so adjusted as to give the requisite neutralization without danger. The soda, of course, decomposes its equivalent of the ammonium salt, giving free ammonia, and the alkalinity of this already weak base is further reduced to any required extent by the presence of the neutral ammonium salt, which by a well-known law diminishes its ionization.

It is not essential that the interior of the skin should be fully neutral, as this is secured by a succeeding process, that of "fat-liquoring." The fat-liquor is a solution of a nearly neutral soap, in which a small quantity of oil is emulsified, and in which the skins are drummed. The oil and soap penetrate, coat, and lubricate the fibres, giving softness and additional water-resistance, and convert any remaining traces of unfixed chrome into insoluble chrome soaps. If the surface is insufficiently neutralized, such soaps are formed outside the skin, and adhere to it as a sticky mass, which renders the subsequent dyeing and finishing impossible.

Chrome sole-leathers are not usually fat-liquored, and sometimes not even neutralized, but are dried out and impregnated with a melted mixture of waxes and rosin, which gives firmness and water-resistance.

Several other mineral tannages are possible, and especially those with iron, which forms salts analogous to those of aluminium and chromium, but which have not yet attained any commercial importance.

We may now pass on to notice very briefly what is the oldest and, perhaps, still the most important of tanning methods—the

vegetable tanning process. In principle this is practically the same as was used by our forefathers, though in detail it has undergone great modifications, the most important of which is the use of much more concentrated solutions produced either from exotic materials naturally stronger than proverbial oak-bark, or concentrated artificially by the use of the vacuum pan. A good instance of the latter is the very important "oak-wood extract." Oak-wood naturally is only about a quarter as strong as oak-bark, and can hardly be used for direct tanning, though large quantities of branch-wood, sawdust, and other waste are available. By the concentration of weak liquors, syrupy liquids containing 25 to 30 per cent. of tanning matters are produced, which are suitable for modern requirements. The sources of such extracts were principally Southern Austria and Northern Italy, and their disappearance during the war, together with that of the Turkish acorn-cups, known as "valonia," has led to an absolute famine of tanning materials, and contributed much to the scarcity and enhanced prices of leather.

In principle the process consists in soaking the prepared hides in solutions of the class of organic substances, known as "tannins," which differ considerably in chemical constitution, but have the common characteristics of precipitating gelatine and converting skin into leather, and are very widely distributed in barks, woods, leaves, and even roots. Whether the precipitation of gelatine and the analogous action on skin are strictly chemical or physical processes has been much discussed, but the facts are as follows: Both tannins and gelatine are distinctly colloid in character—that is, they have either very large molecules, or these molecules exist in groups in the liquid, as colloid and not true molecular solutions. These particles are electrically negatively charged, while gelatine and skin fibres in slightly acid solution are positive. When, therefore, the two are brought together, they attract each other by their opposite charges, unite, neutralize, and precipitate. The mechanism of the combination is not different from that of positively and negatively charged ions, such as sodium and chlorine, but it deals with whole molecules or particles instead of ions, and it seems a matter of taste whether we call it chemical or physical. In faintly alkaline solution the skin or gelatine particles, from their amphoteric nature, take

negative instead of positive charges, and in this condition are not tanned or precipitated by tannins. Hence in tanning, faint acidity of the liquors is essential, though what is the *optimum* acidity has not been fully determined, and must depend upon the character of the leather desired. Acidity causes swelling of the fibres which leads to hardness and stiffness, and thus for the softest and most flexible leathers the smallest possible swelling is required, while for sole much more is desirable. The degree of swelling is also affected by the neutral salts, as was earlier explained, so that the solution of the problem does not merely depend on acid-concentration. The minimum swelling is obtained slightly on the alkaline side of absolute neutrality, on which tannage would not be practicable.

While what may be called the first stage of tanning is purely chemical in the sense which has been explained, there comes, at least with the heavier leathers, a stage in which adsorption or surface-attraction predominates, and when a sort of chemical equilibrium has been attained, the fixation of the less soluble and more colloid constituents of the liquors on the surface and between the fibres still goes on and adds to the weight and solidity of the leather, and no doubt in the old and slow methods of tanning earlier in vogue this played a larger part than it now does. The matters so deposited are principally ellagic acid (bloom) and the anhydrides or oxidation-products of tannins, which are only slightly soluble in water, and easily separated from it.

Besides the quickening due to the use of more concentrated liquors, many attempts have been made to quicken the slow diffusion into the leather of the colloid and slowly diffusible tannins. The most successful of these has been by the mechanical movement and bending of the hides in rotating drums and other similar devices, which cause a sort of pumping action between the fibres, and heavy leathers can be tanned apparently well in three or four days which would take as many months by the old diffusion process. It is difficult to say to what extent such processes are in use, as drum-tanned leathers have not a very good reputation, and tanners are not anxious to advertise the fact that they make them, but there is no doubt that large quantities of leather are wholly or partially so made, and within limits this is very justifiable, especially under war conditions.

Much has been talked from time to time of the use of electricity for quickening tanning. Colloid particles are moved by electric currents by the effect called "electrophoresis," and may so be forced into or through leather, and it is pretty certain that tanning can be hastened in this way, though whether to an extent and at a cost commercially profitable may still be an open question.

The "vacuum" process is an interesting method of quickening tanning, and is being used on a considerable scale by the limited company which owns the patent. The hides are suspended in vats, which can be exhausted to so high a vacuum that the liquors actually boil in and round the hides at a temperature not exceeding 75 to 80° Fahr., and the interchange of liquor so caused consiberably increases the rapidity of tanning. The process has little in common with the vacuum processes used in forcing preservatives into wood, which in the dry state is filled with air; this expands and escapes under reduced pressure, while hides contain only water, which does not practically expand unless it boils, and hence low vacua are useless.

There are many processes in important commercial use which are combinations of mineral with vegetable tannages, and especially with chrome and alumina, which contain nothing new in general principle, and of which time does not allow description, though the fact is interesting that hide saturated with the one is still capable of absorbing the other, probably because of its amphoteric nature. One of the latest of these is "pyrotan," a combined alumina and vegetable tannage, in which the alumina is precipitated and fixed in insoluble form by sodium pyrophosphate.

A more interesting study is the action of aldehydes, and especially of formaldehyde, in leather-making. Formaldehyde is a volatile liquid which evaporates without residue, so that it cannot well deposit anything on the fibre, according to Knapp's theory. It forms polymerized or conjugated compounds with many substances, and among others with hide-fibre, which it renders insoluble in boiling water. Applied to hide in the swollen condition, it fixes it in that state, and therefore has been applied as a preparation for hides for rapid vegetable sole-leather tannage. Payne and Pullman patented a method (1898) for its use as a tanning agent in conjunction with sodium, carbonate,

and other alkalies, and very successfully made both imitation buff-leathers for military accoutrements, and soft washable leathers for gloves. Professor Meunier (1912), however, has shown that it is not the alkalinity, but the dehydrating effect of the sodium carbonate, which is important, and that other dehydrating salts, such as sodium thiosulphate, can be used with equal effect. A strong solution of potassium carbonate alone will produce a perfectly supple white leather, which, of course, becomes pelty again by washing, and dries hard and horny. If, however, three parts of neutral formol be added to the alkaline solution, a similar white leather is produced, which perfectly resists washing. The effect of formol is therefore merely to fix the skin-fibre in the condition, swollen or dehydrated, in which it finds it. Formaldehyde can be used in this way in connection with vegetable, chrome, or alumina tannages.

Interesting tannages which may be related to aldehyde tannages are those produced by the action of oils, as in washleather, buff, and buckskin, and the best modes of fur-dressing. Common washleather ("chamois," or "shammy" leather) is a typical example, and is produced by fulling the flesh sides of sheepskins in "stocks" while adding fiish- or whale-oil until the pelts are thoroughly saturated. They are then packed in boxes, where they heat rapidly by oxidation, so that they must be taken out and aired at intervals, not merely to provide fresh air, but to prevent dangerous overheating. The skins turn deep yellow, and are converted into leather by the oxidizing oil, and large quantities of pungent acrolein, or acryl-aldehyde (very lachrymatory), from the dehydration of the glycerine are given off. When heating ceases, the skins are wrung or pressed to remove surplus oil, which is valuable for stuffing other sorts of leather (degras, moëllon, sod-oil), and after washing with soda or potash solution, and fluffing on an emery wheel, are ready for use. Knapp's simple explanation that the process is an isolating and coating of the fibres with oxidized oil products is negatived by the fact that all the latter are saponified, and washed out by alkaline solutions, and also the plausible view that the acryl-aldehyde is the real leathering agent, since Wood has shown that equally good leathers can be made with the fatty acids of oils from which the glycerine has been removed. This does not, however, entirely

negative the aldehyde explanation, since only "drying" or unsaturated oils can be used, and their acids frequently split at an unsaturated bond, giving aldehydes as products. Marine oils are invariably used in practice, but Fahrion has shown that linseed and other unsaturated vegetable oils will also produce the effect, and the very tough and beautifully white Japanese leather, used for brace tabs and the like, is made with rape oil. Fahrion shows that oils must have at least two double linkages to produce this effect (marine oils have three or four), and Meunier points out that this produces a quinonoid structure by oxidation.

Marine oils are largely used in currying vegetable tanned leathers, and if the latter are not fully tanned, produce a sort of supplementary oil tannage very advantageous to the quality. In addition to the present methods of making leathers there are many others possible, and some which have been commercially used on a limited scale. Meunier has shown that leather may be produced by the action of bromine, probably by forming insoluble bromamines, and that the various quinones are quite practical tanning agents, being partially converted into hydroquinones and giving good brownish-coloured leathers. He attributes the action of vegetable tans to the quinonoid bodies already present or formed by oxidation, and has shown that the power of most phenols to insolubilize gelatine is dependent on quinones formed by oxidation. A good many "synthetic tannins" have been patented, bearing no close chemical relations to the natural tannins, but having pronounced tanning properties. Much the most important of these are Stiasny's "Syntans," one of them, "Neradol" being now largely manufactured in this country by Government license under various names, and used in conjunction with other materials for plumping and bleaching, as alone it gives an almost white, but somewhat empty leather. It is produced by condensing sulphonated cresols with formaldehyde. Zacharias long ago showed that many aniline dyes, and especially the methyl violets, will also produce leather if used in sufficient quantities.

Distinguished from these are various colloid precipitates which, drummed into the skin, convert it into leather by coating and separating the fibres according to the old Knapp theory. In the two-bath chrome process the sulphur precipitated on the fibre considerably increases its softness and fulness, and by treatment

with acids and sulphur-yielding compounds without the chrome, purely sulphur leathers may be made. Freshly precipitated alumina has considerable tanning properties, and phosphate leathers may be made by precipitating phosphate of lime in the skin, while most metals giving basic and colloid salts, as for instance titanium, may be used in producing leather. A process for tanning with colloidal silicic acid has been patented by Mr. A. T. Hough (English Patent No. 17,137 of 1915), which seems to give results of considerable practical value.

Probably enough has been said to show that no single theory can account for all the various ways in which leather can be made, and that there is no limit to the varieties which may be produced.

FISH OILS AND THE LEATHER INDUSTRY.*

By H. Schlosssteín.

The most important mateiials used in the producing of leather are, besides tanning extracts, undoubtedly, oil and fats.

They are applied either in their natural state or as a manufactured product prepared, such as to fit best the special purpose for which they have been intended.

The reaction of fat and oils on leather are quite manifold. They might be defined as leather building, (oil-tanning, chamois-tanning) protecting, waterproofing, body-giving (stuffing), weight increasing, softening, lubricating and preserving.

The natural oils and fats in use are mostly fish oils and other animal oils such as whale oil and seal oil, all of which belong to the same class, called marine oils. These same oils, treated, as sulphonated oils, oxidized or emulsified oils (moellons), and lately also as hydrogenated oils likewise find an extensive use.

Among the fish oils used in natural state, we may mention here as first one, cod oil or better, codliver oil, because it is a product of the fish livers, which are under all circumstances the part of the fish body that is richest in oil. Some chemical authorities divide fish oils in two classes calling one "liver oils," and the others "body oils," which is in so far not correct as the body

* *S. and L. Reporter*, 1918.

oils are always compounds of liver oils and body oils, the liver of the fish being never removed previously to the pressing or extracting, except when the purpose is to produce pure liver oils. The process of manufacturing fish oils necessarily affects to a very large extent their quality. Liver oils are usually produced by a steaming process which yields the larger amount of oil contained in the livers. Also the pressing of the livers by means of hydraulic presses is being practiced. The body oils, which are obtained from the whole fish were formerly produced exclusively by boiling the fish with water which yielded only 1/3 to 1/2 of the available oil. This process was improved later on by having a pressing process follow the boiling. It is evident that the boiling process has a tendency to impair the quality of the oil produced, because the organic fiber of the fish body in connection with the water and high temperature will tend to split up the fat into glycerine and fatty acids and therefore decreases its commercial value. The most ideal working conditions would exist if the fish would be subject at a high temperature to a current of steam in the vacuum, which would produce the best obtainable quality of oil. Besides, the pressing and boiling process there is also the extraction process in use, which consists in the extracting of the oil from the fish body by chemical solvents such as naphtha, benzine, tetrachloride, trichlorethylene, carbonbisulfide, etc. In this country naphtha is used nearly exclusively.

The extraction process has the advantage of leaving a by-product (used as fertilizer), which is nearly free of oil, increasing herewith necessarily, the yield. It is also possible, for instance, to work up the presscakes left from the boiling-pressing process by extraction. A commercial draw-back, however, is the dark color of the oils produced. This is partly due to high temperatures used in the process of manufacturing, but to a large extent it is the consequence of the extraction of dyeing principals, contained in the fish body, by the solvents. In cases where the dark color is caused by over-heating and really constitutes a limited carbonizing of the fat molecules, it means necessarily a serious draw-back as regards quality, but on the other side when only caused by animal coloring matter it is less serious, and does not fully justify the antipathy of the trade towards these darker oils. It may be mentioned here that some fish oil extracting

plants are rather careless in handling their products, and leave a high amount of the solvent in the oil, which of course, impairs the quality. Nevertheless, they are in the minority, because in the long run they are the ones who suffer most over this carelessness. The ideal solvents for extraction of oil and fats are Tetrachloride and Trichlorethylene. It is possible that by the use of these solvents the quality of the domestic extracted fish oils could be considerably improved, but until now their high price and the fact that trichlorethylene has not been produced here in very large quantities has prevented their utilization in the domestic fish oil industry.

As previously stated, the fish oil most frequently used by tanneries in this country is cod oil, while in the northern part of Europe, whale oil predominates, and in Japan sardine and herring oil range in first place. The preference of the domestic leather manufacturers for cod oil can probably first be traced back to the fact that this was the first fish oil produced in quantities over here because its manufacture presented the least difficulties, since the raw material, viz., the livers, are very rich in oils. Even only a comparatively short time ago cod oil was the only domestic fish oil besides Menhaden oil which was produced in large quantities and in uniform quality. However, within the last few years, the Pacific Coast fisheries have greatly developed and produce to-day a number of oils equal or superior to cod oil. There has been some prejudice from sides of the old-fashioned tanner against these newer fish oils and some writers even now are still accustomed to distinguish between fish oil and cod oil, unaware of the error so committed because the sacred cod is a fish after all. It also has been a standard doctrine that fish oils are drying oils and cod oil is non-drying, and it has been pointed out that these fish oils as drying oils in moellons and other leather preparations would hurt the leather. We shall investigate in a later paragraph the influence of semi-drying oils in this connection (establishing from the start that there are no strictly drying oils to be found among animal oils), and will compare at present only the drying properties of the different fish oils. As a rule the drying quality of an oil is expressed by the iodine number, which represents the amount of iodine absorbed by an oil, and which, as it has been shown, is proportional to its oxygen

absorbing power. Lewkowitsch finds by comparative tests, that the proportion of iodine absorbing capacity to oxygen absorbing capacity is two atoms of iodine to one atom of oxygen multiplied by 0.632. Applying this formula to fish oils, the iodine number has very often proved to be misleading in establishing their drying qualities, because there are a good many fish oils with a high enough iodine number to class them near to the quick drying vegetable oils, but which show much poorer drying qualities than could be expected. This is probably due to the fact that the iodine absorbing power of fish oil is due mostly to clupanodonic acid, gadoleic acid, erucic acid, jecoleic acid and jecoric acid, and not to linolic acid, as in vegetable oils, and that the solidifying tendencies of these acids are not always proportional to their oxygen and iodine absorbing powers. Therefore, it might be said that, while a high iodine number with fish oils not always means that the oil will dry quickly, it, however, still holds good that an oil with a low iodine number cannot dry or solidify rapidly under the influence of oxygen. As a rule Menhaden oil and certain grades of sardine oil and herring oil shows the greatest tendency to solidify or dry. The iodine numbers give us, nevertheless a comparative scale as regards the fish oils themselves. We hereby give a number of iodine numbers of the better known fish oils: sardine oil 110-190, herring oil 130-155, cod oil 165-170, Menhaden oil 150-180, dogfish liver oil 128-155, tuna fish oil 150-155, porpoise oil 119, salmon oil 160-165. We also mention again whale oil 125-150, sperm oil 75-85 and seal oil 125-145. The wide margin in iodine numbers given for some of these oils is a consequence of the different conditions in which these oils have been produced, and also of the different countries of origin. So, for instance, Japanese sardine oil will show a different iodine number from a Pacific Coast sardine oil, etc. Also very frequently these fish oils are not strictly the kind of oil indicated by the name, but very often are a compound representative of three or four different fish oils.

It is convincingly proved by the array of iodine numbers, that there is a large number of fish oils which have a lower iodine number than cod oil and that only comparatively few have a higher iodine number. If, therefore, the iodine values or comparative drying qualities of an oil were the only measure of its

value, as a leather oil, cod oil certainly would not be in the first line. Of course, it is evident that wherever oil is used for the oiling of leather, with a view of softening same and keeping it pliable, it would be a marked disadvantage if the oil would begin to gum or dry on the leather fiber and by partly solidification would render it stiff and impair its strength and wearing qualities.

Another point which is usually considered in establishing the value of leather oil is the contents of glycerides with a high melting point, which are usually combinations of palmitic acid and stearic acids. Especially fish oils which are to be treated and transferred into different preparations, should be as much as possible free of these higher melting glycerids, for reasons to be explained in a later paragraph. It is not very difficult to remove the undesirable glycerides. It is accomplished by reducing the temperature to a point where the higher fatty acids will begin to settle out, and by filtering the compound. The stearine contents (as it is usually called) of the different fish oils, as they are offered to the trade, depends mostly on the carefulness with which this elimination process of the stearine has been handled, or whether it has been applied at all.

While a few years back, fish oils were usually sold on sample or as "fair average quality" of certain established factory runs, it is now a prevailing custom to sell most fish oils on a basis of free fatty acids (FFA), and moisture, impurities and unsaponifiable (MIU), which is really to be preferred. Newfoundland cod oil and domestic cod oil still are, however, frequently sold on the FAQ basis even to-day. Whale oil is sold as No. 1, No. 2 and No. 3, while other trade denominations are "prime" (mostly with Menhaden oil or indicating less than 7 per cent. acid), "refined," "crude," "pressed" (meaning in connection with the Menhaden oil that the stearine has been removed, and in connection with other fish oils that they have been produced by the pressing process), which need no further explanation.

As regards the color of fish oils, it might be said that certain denomination such as pale, red, brown, light, dark, have to a certain extent acquired in the trade the value of standard expressions, usually indicating just a certain shade, and convey sufficient information to the expert. However, it would be de-

sirable, if fish oils were sold like cottonseed oil on a certain color scale which would eliminate all guess work.

As regards fish oils used in the process of oil tanning (chamois tanning) the ones best fit for this purpose are such which show the greatest oxygen absorbing powers. Sperm oil, for instance, which has a very low iodine number, and therefore is an absolutely non-drying oil, is also absolutely unfit for this purpose. The reason for this phenomenon which usually is not well understood by practical men is, that the tanning effect is not produced by the oil proper, but by the oxidation products of its fatty acid and by aldehydes, which have been produced through the decomposition process of the fat. After the oil has been absorbed by the animal fibre, decomposition will start, and assisted by the organic matter contained in the leather, it will partly split up into fatty acid and glycerine. Parallel to this decomposition process goes an oxidation process due to the fact that the oil is exposed to the air in a very thin layer. It might be mentioned here that fatty acids as a rule absorb only half the amount of oxygen absorbed by the corresponding glyceride. The effective tanning principle, that is being formed in the leather, and effects the transforming of the skin into leather is of dark brown color, of acid nature, and of unknown composition. To a certain extent, it is probably always formed whenever oil is applied to leather, and therefore the effect of oil on leather in all cases, such as in the currying process, etc., must not only be considered a purely physical (as lubricant and softener,) but as a combined physical and chemical, in the nature of a second tannage.

Sulphonated fish oils are used very extensively by the tanning trade. The process by which they are obtained is rather simple, but the changes foregoing in the oil during this process are very complicated and little positive knowledge about them is available. The process has to take place at a temperature under 35 degrees centigrade, and a concentrated sulphuric acid is used. Under certain circumstances, sulphuric acid has a tendency to transform oleic acid, by oxidation, into stearolactone and isomeric solid oleic acid, which have a much higher melting point. However, the presence of higher melting fatty acids is not at all desired in sulphonated oils, and for this reason also it is usually well taken care to start with a fish oil which has as low a stearine content

as possible. A good many sulphonated oils which are on the market show a smaller or larger percentage of higher melting fatty acids in form of more or less sediment, which is a result of a not well enough controlled manufacturing process. It may also be mentioned here that nearly all these sulphonated oils contain a certain amount of ammonia soap, because this increases their solubility in water, and also assists in producing a clear oil. This solubility in water of the sulphonated oils is chiefly due to the formation of sulpho-fatty acids and glycerides. The sulphonated oils of the commerce are usually handled on the basis of moisture contents, which in most cases is between 15 and 25 per cent. Their consistency is always much heavier than the one of the natural oils from which they have been produced.

The oxidized oils used in the leather industry are either by-products of the oil tanning process (chamois tanning) or, since the demand for these products is larger than the supply furnished by this industry, this process is being imitated with a view of artificially producing these oils. As this process is known well enough, it does not need to be described here. The quality of these oils depends to a certain extent on whether the oil has been separated from the leather by pressure or by saponification. In case the product has been obtained by pressure, it consists of a compound of neutral oil, oxidized oil, fatty acids, oxidized fatty acids, water and these partly unknown products which are a result of the oxidation of the acids and their reaction on the leather tissue. These are really of the greatest importance because they form the effective principles of the compound, and being slightly soluble in water are strong emulsifying agents. In case the oils have been obtained by saponification which means that the fat and acid in the leather has been transformed into soap and later on by a treatment with a mineral acid, again been decomposed, they contain a higher amount of acid and generally are of an inferior quality, owing to the effect of the mineral acid, on the fat molecule. The process of manufacturing oxidized oil is now also carried out entirely independent of the oil tanning method by treating the oils with ozone or air under admixture of water. So, for instance, oil and water are sprayed from opposite directions into a chamber containing ozone or also the reversed may be used and there are hundreds of other different applications of

the same principle possible. The oxidized oils so obtained are of very heavy consistency and contain a certain amount of moisture (usually around 15 per cent.) and also all those oxidation products the beneficial influence of which on the leather fibre has been described in a previous paragraph. Trade denominations for these oxidized oils are moellon and sod oil. The oils which are best fit for the producing of these products are the oils which absorb the highest amount of oxygen and therefore, will produce and contain the highest amount of effective principles. A good moellon shows the following qualities:

1. Should have only traces of iron, less than 0.05 per cent.
2. If exposed to dry heat of 100 degrees centigrade for ten hours, it should turn to a jelly-like mass, but not form a film.
3. Shall have no tendency to congeal in form of large crystals.
4. On moist leather, it should be absorbed in thirty minutes.

It sometimes happens that leather treated with moellon will show after some time a slight white secretion that spoils the finish. This has been attributed by some writers to a drying process, and indeed it is known that hydroxylated fatty acids occur in form of fine white crystals. If this was the case, however, moellon made from cod oil as a rule would show a greater tendency to produce this secretion on account of its comparatively large oxygen absorbing power. This white secretion is probably a consequence of too high a stearine content in the moellon, and is not effected by the fact whether it has been made from cod or fish oil. It may even be mentioned here that Bull and Hartley have proved the existence of dihydroxypalmiticoleic acid and of dihydroxylstearic acids in cod oil as an indirect oxidation product, both acids appearing in form of white crystals. Also it is quite obvious that this white secretion cannot be caused by a drying process of the oil itself because the oxidation products or films of such oils would be of brown color.

Within the last few years the utilization of hydrogenated or hardened oils has also been considered and to a certain extent been adapted by the leather industry and we may expect important developments in that respect in the near future. The hardening process of oil consists in the transforming of the oleic

and related acids into palmitic or stearic acid under the influence of hydrogen which is bound to the oil by means of a catalyzer. The chemical change produced by the hydrogenation process on the oil consists in the saturating of the unsaturated fatty acids, and, therefore, hardened oils, in advanced state, have a low iodine number. These hydrogenated oils can be produced in any degree of hardness or consistency and especially the combination of the sulphonating or oxidizing process with the hardening process promises to show some very interesting results.

It is to be expected, and hoped for, that with the increasingly larger demand for fish oils from the leather industry, new sources of supply will be opened with the erecting of new fish oil factories in order to meet the increased demands of this important industry, and prevent prices from reaching too high a level. The bureau of fisheries in Washington is doing good work in promoting and assisting the establishing of new factories, which is surely fully appreciated by the entire leather industry.

DRENCHING.*

By J. R. Blockey, M.Sc.

The term drenching has lately been rather loosely applied and has been used to describe almost any process applied to limed pelt with the object of removing the lime. Thus it is sometimes used to describe a process of deliming using merely an acid. Many of the processes incidental to tanning which are included in the term "wet work" or beam-house processes are described by somewhat vague terms and the names bating, drenching and deliming are often used promiscuously. All three really denote quite different processes although all three have as part of their object the removal or neutralization of lime. By deliming is meant merely the process of removing lime without any other important side reaction. This is usually accomplished by one of the common organic or inorganic acids such as formic, lactic, sulphuric or boric acid. To define this process still more rigidly it might be called acid deliming to distinguish it from those processes using the ammonium salts such as the chloride.

* *S. and L. Reporter,* 1918.

Bating is a general term to include those processes which are given to skins before tanning and which involve the use of fermenting substances. Originally the name was given to the process involving the use of excrement. (Bating included the processes using hen and pigeon dung whilst puering was given to the process using dog excrement.) Nowadays bating is used to include both these processes and also all those processes which involve the use of the numerous substitutes which have been devised to do away with the natural materials.

Drenching, although a fermentation process, is quite a special one and will be taken in the following article to refer only to the process consisting of treating the skins in a fermenting infusion of bran.

Drenching is usually applied to skins which have already been bated or puered so that the skin will be alkaline although some of the lime will have been neutralized by the bating liquor. In some cases, however, bran drenching is applied to skins which have not previously been bated, for instance in the manufacture of calf kid it was customary to omit bating before drenching.

The actual process of drenching is not subject to very wide variation, although there are several quite distinct methods of preparing the drench liquor before the skins enter it. Perhaps the commonest method of making up the liquor is to mash the bran in the vessel which is to be used for drenching, with tepid water, that is at about 100° F. (36° C.). The amount of bran is calculated on the amount of water and may vary from 5 to 10 lbs. per 100 gallons or reckoned on the weight of skins from 5-10 lbs. per 100 lbs. of skins. Having been well stirred, the goods are placed in the liquor which will probably reduce the temperature to below 30° C. Fermentation of the bran rapidly sets in and continues rather vigorously for about 24 hours. The fermentation is accompanied by the evolution of gas which rises and causes the skins to float to the top. The skins are usually pushed down again under the liquor and allowed to rise once again, although some workers remove them at the first rise, while others allow them to rise three or more times. The rising of the skins is taken to be the sign that the drench is "working" properly. The completion of the process is a matter of choice. Some workers allow the skin to rise a definite number of times, and

take that as a criterion of the correct extent of drenching. Other workers judge by the feel and appearance of the skins and this method is much to be preferred although it is a matter of expert knowledge and experience. Prof. Procter has given the following description of the feel and appearance of properly drenched skins. "A certain sign of sufficient drenching is the appearance of small blisters on the grain, caused by the evolution of gas in the substance of the skin. When these are seen the drenching should be discontinued at once, as otherwise the blisters will increase in number and burst through the grain, causing minute holes or "pricks" (one of the many forms of the complaint called in German "Pikiren"). When a bubble of air is enclosed in a fold of the sufficiently drenched skin and pressed, it raises the grain without actually separating it from the substance of the skin. The properly drenched skin also falls easily in folds when held between the hands either lengthways or crossways, and if thin, the skin tightly stretched over the hand shows grains of bran underneath it as little lumps, round which the skin clings to the hand. The drenched skin should not be transparent, but white and soft, and when pressed should retain the mark of the finger. Some experience is required to determine with certainty the point of sufficient drenching, which of course varies with the character of the skins and the kind of leather which is to be produced; and the feel of the skin to a practised hand is one of the most important criteria."

Another method of making up the drench which is practised in continental Europe is to mash the bran with boiling water, allow to cool for several hours and then to separate the liquor from the bran and use the liquor for the drenching of the skins. It will be shown later that by this method quite a distinct difference is made in the changes which occur.

A third method is the so-called sweet drench which is often used in France and Germany, in which fermentation with the production of acids is not allowed to take place. By this process the skins are merely paddled in the freshly made mixture of bran and water for two or three hours. Since no acids are formed the process is called a sweet one and the action is mainly a mechanically cleansing one and not a deliming one.

Still another variation in the method of making a drench is

one described by Wood in which the bran is soaked in cold water for several hours and then hot water added to bring the temperature up to 50° C. and again allowed to cool to 35°C. A small quantity of an old drench liquor is added to start the fermentation, which is allowed to proceed for about two days. Acid is formed and the amount reaches its maximum at the end of two days. At this stage the bran is strained off and only the milky liquor is used for drenching. As will be apparent later this method is merely a glorified acid deliming process and some of the special virtues of the bran drench are not utilized.

By the process first outlined it is usual to leave a little of an old drench in the vessel. This is to ensure that the proper fermentation shall take place without delay. As the process is usually carried out in wooden vessels this precaution is scarcely necessary, because the interstices in the wood will always contain sufficient of the fermenting medium (whether organized or unorganized) to inoculate the new drench.

Something of the effects of drenching will be gathered from the description just given of the judging of the correct completion of the process. One of the most obvious effects is the cleaning of the skin which becomes whiter and more uniform in color. The section is also more opaque than before and the skin has a curious leathery appearance when squeezed between the fingers.

The main object of drenching is to complete the removal of lime. Drenching is usually given to skins which have been already bated or puered. They are therefore still alkaline in reaction although they contain less lime than before bating. The drench helps to remove the last traces of lime and this is its main function. Along with this deliming action there is the cleansing effect which is brought about by the mechanical action of the bran particles, although this function cannot be brought into play in those modifications of the process in which the bran is separated from the liquor. This cleansing action is particularly valuable upon bated skins which are often contaminated with dirt and it is useful in lightening the color of the final leather. There is also the slight swelling effect produced by the acids.

The drench does not reduce or pull down the skins in the same way as bating or puering and there is not the same dissolving action on the skin substance. Drenching therefore has

not taken the place of bating or puering entirely, but in those cases where the solution of skin substance is not desired, that is in those cases where the main effects derived are acid removal, softening and cleaning of the skin, the drench may very often be successfully used to replace the bate or the puer, and even in the cases where bating is thought necessary the supplementary action of the drench may often be worth while.

One reason for the substitution of drenching for bating is that of safety. There is much less danger of over-stepping the point of damaging the skin by drenching than by bating or puering. The reason for this will be apparent when describing the mechanism of the drenching process. Something has already been said about judging the completion of the drenching process although an error of judgment here is nothing like so serious as in the case of bating. The dangers which are liable to occur with drenching are not due so much to over drenching as to outside influences. If bating be allowed to proceed too far the whole skin tissue may be ruined, while with drenching the only serious form of danger is likely to occur when the drench is not working properly, that is, when the wrong fermentation is taking place. In other words the ferments which produce the real drenching action do not attack the skin substance. This safety of drenching compared with bating has been partly responsible for the gradual replacement of the latter process by the former.

Drenching is one of the few processes of tanning which have been elucidated. Most of the processes incidental to tanning, such as liming and the actual tanning, are still not thoroughly understood, but drenching has been the subject of exhaustive research and the whole mechanism of the changes has been brought to light. Most of this work has been done by J. T. Wood, who has classified the changes which occur in drenching into three divisions:

1. The mechanical cleansing action of the solid bran particles.
2. The deliming action of the acids.
3. The distension of the fibres by gases.

The mechanical cleansing of the surface is brought about by the solid particles of bran which absorb the surface dirt. This cleansing action is akin to the familiar housewife's method of

cleaning stains from garments by means of bread crumbs. Bran itself may even be used for a similar purpose in another connection; the removal of mould from finished leather. The mechanical action of the bran in drenching is usually mainly effected by means of the paddle which forms a convenient vessel for drenching. The first part of the process may be carried out in the bottom of the paddle and when the skins have risen a sufficient number of times the paddle may be filled with water and the skins turned in it.

The cleasing action is most useful for skins which are to be finished in light colored or fancy shades, and is most necessary for skins which have been bated or puered in natural bates because these are usually more prone to dirt on the surface than skins not so treated. That this is so is proved by the fact that skins which have been bated in an artificial bate which is cleaner than the natural bate, may be drenched quite successfully in a liquor from which the solid particles of bran have been removed, while on the other hand, skins which have become soiled in a natural bate would not be sufficiently cleaned in a drench liquor without the solid particles of bran.

The rising of the skins in the drench is due, as already stated, to the evolution of gases. Apart from the obvious effect of causing the skins to rise in the liquor there are less visible effects produced in the interior of the skins. The gases which are formed by the fermentation of the broken down products of the starch from the bran may be present between the fibres and cause them to be more finely separated so that the absorption of the acids and later of the tanning agent may be facilitated. In a normal drench the distension of the fibres is not visibly pronounced although its effect may be appreciable, but in certain cases of faulty drenching, particularly where the evolution of gas is too rapid or too violent, the distension may assume proportions large enough to damage the skin. For instance one of the most frequent of the damages caused by wrong drenching is called "pinholey drench" and is due to excessive evolution of gas, which collects in the spaces between the fibres and especially just beneath the grain. The gas may burst through the grain surface and produce small holes which has given the name pinholey to this defect. The effect of this distension by the gases is sometimes exagger-

ated. for example Eitner has stated that the main effects of drenching are due to dynamic phenomena caused by the gases formed by the fermentation of the bran. Wood's researches have shown that much more important changes than this occur.

The production of acids by the fermentation of the bran and the action of the acids upon the skin form the most important part of the process of drenching. The skins to be drenched usually contain a certain amount of lime whether they have been bated or not. If the goods have been bated in a natural bate they will still be alkaline although containing less lime than before bating. The function of the acids produced in the drench is to neutralize this lime and to produce the slight swelling effect already mentioned. The changes by which the acids are formed are complicated but they have been carefully elucidated so that this question serves as a model of the methods which may be applied in the unravelling of the reactions which underlie the complicated processes of tanning. As already mentioned it was J. T. Wood who carried out the work and the following figures are taken from his publications.

The composition of bran is complex but it is necessary to have a rough outline of it in order to understand the changes which occur during the breaking down of the bran by the fermentation.

An average composition is the following:

	Per cent.
Water	14
Starch	44
Fibrin	15
Lignose and cellulose	17
Fat	4
	6
	100

The first action which takes place is due to enzymes which attack the starchy matters in the bran. The enzyme first breaks up the starch into rather simpler substances and then the bacteria attack these new products and yield the acids. The enzyme is present in the bran although the bacteria gain access from outside sources. It is a very interesting type of fermentation and closely resembles one of the most widely studied of all enzyme actions, that of breaking down of the amygdalin contained in bitter al-

monds by the enzyme emulsin. The interesting feature about these enzyme actions is that the fermenting medium (the enzyme) and the substance which is fermented (the starch or the amygdalin) are both present in the original substance (the bran or the bitter almonds) and that in the natural state these two substances do not act upon one another but that when the bran is mashed with water or the bitter almonds crushed, the enzymes begin to break up the starch or the amygdalin. When bitter almonds are crushed in a little water, the emulsin breaks up the amygdalin into three substances, glucose, hydrocyanic acid and benzaldehyde, the last of which produces the familiar smell associated with bitter almonds. Similarly with bran, the enzyme which is called cerealin exists along with the starchy matter in the bran but only breaks up the starch when the bran is smashed with water. In both cases the enzyme and the substance upon which it acts are present together in the parent substance and this may seem strange although it is often found to be the case. It is perhaps to be explained by the formation of living substances which is always of a cell-like structure, and which keeps the enzyme and the substances acted upon separate from one another. The two substances may be in separate cells. In the natural state the substances may therefore co-exist without action upon one another and it is only when the parent material is crushed or bruised that the cell structure is broken down and that fermentation sets in. A familiar instance of the same thing is the bruising of an apple which causes decomposition to set in which spreads throughout the apple whilst the same apple without the bruising would probably keep sound for months.

The enzyme in bran is called cerealin and is only present in small proportions. The chief characteristic of enzyme action is that a very small quantity of the enzyme is sufficient to decompose a very large quantity of the substance acted upon, without itself undergoing any change. The action is usually likened to that called catalysis in inorganic chemistry in which the catalyst enables a re-action to occur without itself being used up or destroyed in the process. In another sense it might be regarded as similar to a lubricant which allows the reaction to proceed without itself being destroyed.

The action of the cerealin upon the bran is to break up the

starchy matters into dextrin and glucose but it does not carry the decomposition any further than this and without some further decomposition the correct drenching effects would be lacking, since it is only during the further splitting up of the glucose and the dextrin that the acids necessary to produce the drenching effects are formed.

This further splitting up is brought about by bacteria, but it is not until the enzyme has produced the glucose and the dextrin from the starch, that the correct bacteria can begin to operate, which they do by splitting up the glucose, etc., into the various organic acids. The bacteria either gain access from the air or are introduced by the skins, or when the process is carried out in the same vessel there will always be sufficient bacteria present in the sides of the vessel to inoculate the new bran infusion. In this respect drenching is similar to puering or bating but differs in the fact that the bacteria in drenching act upon the bran and not upon the skin substance, whereas in bating or puering the bacteria and their products hydrolize and decompose the actual fibre. The bacterial action of the drench is due to a specific organism which Wood has called Bacterium furfuris and which he has studied exhaustively. This bacterium is closely allied to the large group of bacteria called coli which are largely responsible for most putrefaction processes. The fermentation of the glucose and the dextrin in this case is an example of what is known as symbiotic fermentation in which two series of bacteria work together to produce certain effects. These two series of bacteria are dependent upon one another or produce effects when present together which are impossible when present alone. In this case it was found that when pure cultures of the bacteria were made, the colonies were of two kinds although the bacteria in the two sets of colonies very closely resemble one another when examined under the microscope both as regards shape and size. The bacteria were so similar that one would almost conclude that they were identical but this was disproved by further examination.

Both bacteria can ferment glucose with the production of acids but the proportions of the various acids produced differ very much not only in the cases where pure cultures of the two kinds are used, but differ also from the proportions of the acids produced when both bacteria are present together. The fermen-

tation produced by the two together is very different from that produced by either of them separately. This was confirmed in the tests made on skin. The amount of acid formed is much higher when the two are present than when only one is present. It seems that the two bacteria, although so similar in appearance are really different in effects and that the two supplement one another in some way.

As these bacteria are so similar Wood has named them Bacterium furfuris A and B.

When the enzyme cerealin has broken down the starchy matters of the bran into glucose and dextrin the bacteria then breaks down the latter products into acids together with the formation of gases. The acids produced are, of course, organic ones and consist mainly of lactic, acetic, formic and butyric in the following proportions:

	Per cent. of acid in drench liquor
Lactic acid	0.0791
Acetic acid	0.0240
Formic acid	0.0031
Butyric acid	0.0013
Total	0.1075

The total amount, therefore, represents just over one pound per 100 gallons. These figures give a typical analysis of the drench liquor during the period of working and do not represent the total amount of acids actually produced during the fermentation, since some of the acids will be absorbed by the skin and neutralized by the lime contained in the skin as it is being formed.

In some cases the amount of acid present has been found to be as high as 0.3 per cent. Lactic and acetic acids are mainly responsible for the effects. Butyric acid, although only present to a small extent in the normal working of the drench may in abnormal cases become the prepondering acid and then gives rise to the trouble known as the "butyric acid tanning."

The fact that the acids are produced gradually during the fermentation of the bran gives the natural drench an advantage over a similar mixture of acids made artificially. In most processes of tanning gradual and smooth changes of condition and reactions are to be preferred to rapid and violent changes. For instance, in vegetable tanning, the strength of the tan liquors in-

creases by a large number of small changes rather than by one or two large changes. Similarly, in ordinary acid deliming, it is usually thought better to add the total required quantity of acid in instalments than in one amount. In drenching, the acids are produced gradually, and as they are being produced they are acting upon the skins. This is a better plan than would be the sudden application of the sum total of all the acids produced by the fermentation of the bran.

J. T. Wood regards this deliming action of the organic acids as the main effect of drenching and he has produced the desired effects of a bran drench by treating skins in solutions of acids made in the proportions and concentrations outlined above. Of course the distension of the fibres by gases and the mechanical cleansing effect of the solid bran particles are absent. Where the skins have been kept clean as in the case where an artificial bate has been used instead of a natural one, the latter cleansing effect is not so essential.

One reason for the popularity of bran drenching as a substitute for bating lies in the safety of the process, which under ordinary circumstances and with ordinary care will follow the normal course outlined. There are, however, one or two abnormal ways in which the fermentation may take place. One of these has already been referred to under the name "Pinholey" drench in which there is an excessive and violent evolution of gases which collect in the spaces between the fibres just under the grain, and which burst through in small pinholes. A similar effect may also be produced by foreign or wrong bacteria which may have liquefying properties. These bacteria may congregate in colonies on the grain of the skins and produce small holes.

The most serious abnormal working of the drench is that associated with the production of butyric acid. In normal conditions traces of butyric acid are formed in the drench but under certain abnormal conditions the formation of butyric acid may quite overrule all the other acids, and its smell (which in correct drenching is not perceptible) becomes most pronounced. This is a very dangerous condition and the skins may be ruined if not taken in hand soon enough. The strong smell may be taken as the first sign. The skins rapidly begin to swell and they become transparent, gelatinous and finally they liquefy and are dissolved.

The butyric acid tanning is most common in very overcast, thundery weather but the exact cause and nature of the reactions which occur are not clearly known.

At the first sign of the butyric acid working, the skins should either be removed and immersed in a strong solution of common salt or salt should be added to the liquor. The combined action of the salt and the acid produces a pickling effect and reduces the swelling. In subsequent processes it should be remembered that the skins have been virtually pickled and that the precaution of adding salt to the early tan liquors is a wise one. The salt also reduces the effect of the wrong fermentation but the liquor should not be used again. The vessel should also be carefully sterilized from the action of the defrauding bacteria by steaming out.

The fact that butyric acid is produced during this fermentation and that at the same time the skins become ruined, should not prejudice the tanners' mind against butyric acid for other purposes, such as deliming. Butyric acid when added artificially is quite safe since the amount is under control. In the butyric tanning of the drench the amount of acid produced is quite out of control and in addition to this the damage is probably caused by other things than the butyric acid. The butyric acid may be regarded as a product or sign of the damage rather than as the main contributory cause.

In both the correct normal working of the drench and the butyric tanning just described the fermentation is an acid one and the liquor remains acid. Sometimes a wrong fermentation sets in, in which the liquor becomes alkaline. This is due to another type of bacteria which have the power of liquefying the skin substance. The skins, instead of swelling, become fallen and the liquor becomes black and foul smelling. The remedy recommended by J. T. Wood for skins which have been through such a drench, is not to add salt to the liquor as with the butyric fermentation, since in the absence of acid the pickling effect would not be produced, but to remove the skins entirely and immerse them in a proper acid and salt pickling bath. The drench vessel should of course be thoroughly scalded to remove the wrong ferments.

Sometimes when the skins are left too long in the drench the

effect is excessive and the goods become empty so that when leather is made from them it is spongy.

Perhaps a word should be said of the changes which occur in the other methods of drenching which are sometimes used. The changes already described, refer to the most common method of drenching in which the bran is mashed with tepid water and the skins immersed in the infusion of the bran and water.

Another variation is the so-called sweet bran drench which is common on the continent. In this case fermentation is not allowed to proceed, so that no acid is formed, hence the name "sweet." The skins are merely paddled in the mixture of bran and water for one or two hours. The action of the acids in distending the fibres and in completing the removal of the lime cannot take place, but the mechanical cleansing action of the bran particles occurs and is accompanied by a marked softening effect.

Still another variation is the one described by the Wood, which is a sort of compromise between the normal method and the one first described. In this method the bran is allowed to soak in cold water, hot water is added, the temperature is brought to 35° C., and then a small quantity of an old drench liquor is added. Fermentation soon sets in, as in ordinary drenching, and in about two days the production of acids is at its height. The solid bran is removed by straining and the milky liquor is used as the drench medium. In this case the acids are not formed in contact with the skins, so that the advantage of the gradual production of the acids is lost. Similarly the cleansing action of the solid particles of bran is also missing. The process in fact is really a complicated system of acid deliming.

Some workers mash the bran with boiling water instead of with cold or tepid water. In Germany, for instance, solid bran is separated from the liquor, which alone is used upon the skins. The bran may also be mashed with a small quantity of boiling water and then cooled down to about 30° C., and the skins immersed in the infusion. If the bran be mashed in tepid water the starch is broken up into dextrin and glucose, which are then further broken up into the various acids. But according to Wood, if the bran be mashed in boiling water, the starch is not broken up in the same way and different fermentations will then occur.

ALUM TANNED BOOT LEATHER.*

By F. T. Howard.

Alum, or tawed leather, is not tanned hide or skin in comparison with vegetable or chrome tannages, but is more correctly a pickled product. The alum and salt used may be washed out of the pelt without much difficulty, or the so-called leather may be further treated with vegetable tannins or chrome to produce a good resulting leather, suitable for all the purposes to which the hides or skins dressed without alum and salt might have been used. The principal uses of pure alum leather is for laces in belt making and certain combing leathers, also in some picker bands. Without the addition of some additional materials, it is not of much value for other work, being too thin, but with the additional treatment of flour, egg yolk and oil, substance and softness is imparted to the alumed pelts, rendering their use possible for gloves—and at one time most extensively for boots and shoes.

With the advent of chrome leather, calf kid was displaced for boots to a large extent. For one reason, it is not a water-resisting leather; in fact, it is the reverse, as its tendency is to gather and retain moisture, and this probably accounted more for the falling off in the consumption of this class of boot material than any other reason. However, fashion may again hark back to kid for boots, and the method of its production may therefore be of some value if placed on record in a technical trade journal.

The skins used comprise English market calf of all weights, foreign salted calf skins, and sometimes dried ones, though dried skins are not so favored as the wet salted ones. For the large size or "monster kid," as it was termed, Continental veal skins weighing 20 lbs. to 25 lbs. each on the average were held in high esteem, the pride of place being given to wet-salted Paris veals, which fully deserved the distinction.

The first stage follows the usual routine of the tannery, viz., soaking in water to wash out salt, blood, and any adhering foreign matters. It is advisable for this leather to classify the skins into sizes and weights as a precautionary measure, to ensure each skin receiving more regular treatment in after processes. The thin skins are thus preserved from too much liming, as the thick

* *The Leather World*, Nov. 14, 1918.

ones may be given just as much time as necessary in the pits without detriment to the thin stock. As a safe measure to ensure even and regular liming, the stock is broken usually over the beam from the soak. All particles of adhering flesh left on by the butcher should be scraped off the hide, so as to expose all the true pelt to the action of the lime. Liming follows the usual course in the tannery, commencing with a used or weak pit and following on with stronger ones, until the hair is found to slip easily. The skins are thrown hair downwards upon the surface of the lime and water in the pit, in such a way that they are well spread out. As each one is thrown in it is pushed downwards with a pole, *applied to the outer edge and not the middle of the skin.* The pits should be drawn and set daily for the first few days to allow every skin coming into contact with the lime. Later every alternate day is sufficient. If the drawing of the pits is neglected, unequal liming follows, accompanied with deep-set wrinkles, which are very difficult, even impossible often, to remove in after processes.

Unhairing and fleshing follow. With the heavy skins, which will give a usable flesh, the band splitting machine is used to cut off a flesh after the unhairing is done. As this flesh finds its way as a rule into vegetable tanned leather, and often figures as rolled in-soling, there is no necessity to flesh the skin if they are to be split.

Following, the stock is scudded out of warm water. This consists of working on the grain, usually with a slate or scudding knife or by a suitable machine. All short hairs must be carefully worked out and the scurf removed effectually, but great care is needed not to damage or scratch the grain in the slightest, as this will be seen in the finished goods and depreciate their value.

The stock is now washed in a revolving tumbler with running water for fifteen minutes. It is not necessary nor advisable to wash out the lime, and to attempt to do so produces papery thin leather through loss of gelatine.

The bran drench is used without bating to prepare the stock for aluming. The quantity of bran used is generally about 2 to 3 per cent. of the drained weight of skins. Wood or stone pits, or large tubs may be used, but they should be kept scrupulously clean to ensure correct fermentation ensuing. The bran

is thoroughly mixed with warm water in a separate tub, then added to the water in the pit, temperature about 90° F., and the skins thrown in, each skin well spread out, so that good contact with the bran is ensured. The pit is covered with boards and canvas to retain the heat.

The drench is usually "set" about four o'clock in the afternoon. By ten o'clock the skins will have risen to the surface by reason of the carbon dioxide gas produced in fermentation. They need to be gently forced downwards and the pit stirred. Next morning on arriving to work the same process is necessary.

The drenching is complete in thirty-six hours. It may be accomplished quicker, but the result is not likely to be as satisfactory. The fermenting bran produces lactic acid principally, and this, formed slowly with the lime present in the skins, forms calcium lactate or lactate of lime, which is soluble in water; but in forming this salt there is also given off carbon dioxide in a gaseous form and under a certain amount of pressure, as it is formed inside the hide tissue. In forcing an outlet, it opens up the skin fibres in minute channels, which in turn allow afterwards the tannin solutions to penetrate the hide more readily. The same thing happens with the use of sour liquors in the preliminary plumping of vegetable tanning. Of course, this is only one of the causes that are present to assist tanning.

The drenched skins are now submitted to a dressing of egg yolk, oil and flour. The yolk of eggs is composed of roughly 30 per cent. of oil, enclosed in very minute cells of albumen. The oil, with water, forms a complete emulsion, which makes egg yolk an ideal fat-liquor for the leather dresser. Egg yolk is, however, very expensive, and to reduce the cost recourse is had to the addition of suitable oil to take the place of a portion of the egg oil. Olive oil is perhaps the best, or more correctly the nearest approaching egg oil in its characteristics, but the leather dresser generally uses a clear neatsfoot oil, one that does not set above, say, 40° F. Lard oil is preferred by some. Calf kid is required somewhat greasy, so oil may be used. The quantity varies according to the determination of the dresser, but as a guide it may be taken that 1 per cent. of egg yolk is used, calculated on weight of drenched and drained skin. If 30 per cent. of this yolk is oil, then by whatever amount the egg yolk is re-

duced in quantity, the loss of oil must be made up by the addition of other oil.

To the egg yolk is added flour. The best wheat flour gives the best results. Investigation has shown that the gluten of the flour is the portion which is retained by the skin, but the starch is a necessary quantity, as it separates the gluten into small particles, which enables it to penetrate the skin tissue and become closely combined with it, giving to the leather plumpness and substance, while the egg yolk gives the desired softness. The amount of flour may be calculated at 8 per cent., but this is subject to alteration, depending upon the skins under treatment. Well-grown skins do not need so much flour to plump them as loose flabby stock.

The flour, egg yolk, and oil is mixed carefully with warm water into a semi-liquid consistency, and in a small tub, which is placed in front of a tumbler. A skin is placed half inside the tumbler, the remaining portion hanging down to the tub in front to prevent the waste of any of the mixture. Skins are dipped into the mixture and carefully placed inside the tumbler until all the mixture is inside. If any skins remain they are thrown into the tumbler, the door secured as quickly as possible, and the machine started to revolve. In thirty minutes or so the mixture will have been absorbed, and without stopping the tumbler a tawing solution of alum and salt is poured in through the axle.

The holes in either axle should be at least two inches in diameter, and kept clean to allow air to pass through the drum freely, otherwise heat is generated, and the confined heated air increases the pressure in the drum, which arrests the free penetration of the various ingredients into the skins. Very poor leather has often resulted from neglect of this simple precaution. Often the fault, as disclosed in the finished warehouse, is explained by saying the leather is "alum bound," whatever that may be. Perhaps the skins had become acid swollen, because of too little salt being used to correct this. As a rule, 6 per cent. of alum, with double the amount of salt, boiled together and used warm, is in general use.

Next the tawed skins are placed in tanks, flat, without pleats, or if necessary only one, and the liquor remaining in the drum is poured over them. In these tanks they remain five or six days

to complete the thorough penetration of the skin. From this the stock is drained, and each skin is thrown separately over a pole, avoiding pleats, in a very hot stove to dry.

When flint dry, the skins are removed with care to avoid the hard edges scratching the grain of other skins, and are piled in a room through which a current of air may pass. Protection against rain only is really needed. Here they remain to age as long as possible, but usually three weeks to one month. From this the skins are dipped in cold water (warm in winter), and formed into piles. After a while the water penetrates, and the goods may be folded. They are then packed closely in a suitable box and planks placed over them, upon which are put heavy weights. In twelve hours the stock will be in a suitable condition to stake. This should be done well, otherwise small dry patches are left which refuse to take water or dye afterward.

Staking completed, the goods may be further dipped in cold water to damp sufficient to shave. Hand shaving is generally adopted, as opening the skin more than the machine does. The shaving having been done, the skins are taken while still in the damp condition, and placed in a drum with a small quantity of warm water, in which they are run three minutes, when the excess of water is run out of the drum. This is to secure a thorough wetting of the stock preparatory to re-egging. The amount of egg yolk, flour, and oil may be taken at the same percentages as previously given, but this time the calculation is made upon the weights of shaved leather, so that the weight of each ingredient is less than for the first dressing.

The use of salt in re-egging is not to be encouraged. It is only used to obtain softer leather, which really means to retain moisture in the skins to prevent them becoming hard; in addition, it causes trouble by coming out on the surface of the finished stock, or "sprouting," as it is called. One hour to one hour and a half, regulated by the thickness of the skins, is sufficient to drive the mixture into the skins. From here the skins enter the dyehouse, where they are laid straight on a table until the egg mixture has become absorbed and the water drained away.

At one time the demand was for a white flesh and black grain, which necessitated table dyeing or staining. The table had a rounded top with a gutter on either side to take the water away.

A skin was placed thereon and lightly put out with lignum vitæ slickers. The prepared dye is brushed on until a sufficient depth of color is obtained, when a solution of copperas is poured over the skin to strike the black, followed by a good washing with water. Previously to brushing on the dye, the skin is brushed over with a mordant. The favorite one is stale urine, but equally effective and more cleanly is carbonate of ammonia, or a good washing powder in solution. The dye is a strong solution of logwood extract, quite dissolved, to which is added fustic extract to correct the too blue tint. To 5 per cent. of logwood extract may be added 1 per cent. of fustic or less, with alternately the amount made up with quercitron extract. This will give a good black.

The alternate method is to ridge the skins, that is, to fold a skin so that the pleat extends from neck to tail, grain out. The pleated skin is lightly put out on the table and horsed. A dozen skins are placed in a shallow dye vat, into which the dye is poured warm. A man on one side dips a pleated skin under the dye, and the man opposite places it on his side the vat until all the dozen have passed through the dye. The process is reversed again and again until the dye is deep enough. The liquor may become exhausted, in which case it is run off and a fresh supply obtained. When dyed, the skins are dipped into a solution of copperas, and again into clean water. The skins before dyeing are mordanted, as with table dyeing, only the same method of application is adopted as dyeing in the vat.

After dyeing, horse the skins and allow to drain, then set out on glass-topped sloping tables, using no more pressure than necessary. Only the grain is set out. When set out, cover with clear oil, using a pad, and place the skins over poles in a warm stove to dry. The dried leather is next placed in a cool airy room to mellow for a few days. The stock is then taken and plunged into warm water for a few minutes, and is then placed folded into boxes to get into condition for the final staking. It should be ready if left overnight, when it may be staked.

After the first staking hang the skins to dry a little in a stove, but before becoming dry, stake again. Follow with an emery wheel or shaving machine on the flesh, and again stake. This should be sufficient. The skins should be dry before the last

staking, and should be given an application of dissolved soap to the consistency of a jelly on the grain before the final staking, then stoved and staked.

The stock is now ironed to obtain a fine grain. The irons used are not too heavy, but rounded at either end, and are about 6 ins. by 3½ ins. The edges are kept fairly keen, as they are used to set out as well as flatten the grain. The butt half is placed upon the ironing pad, and the method is to run the iron from the table edge to the tail of the skin, upon which a flat weight is placed; then from the centre to the right shank, which is weighted. The other shank is treated likewise, followed by the putting out and ironing of the remaining portions. The neck half is then ironed.

Lastly, a composition of soap, oil and beeswax, formed into an emulsion, is carefully applied with a pad as a finish to the leather. If to be sold by measurement at a price per foot, it is usual to put the skins through the machine before applying the composition, so that no marks may appear on the finished stock.

THE PAST AND PRESENT VALUE OF LEATHER BELTING.*

By F. R. Parsons.

Users of power generally are, because of enhanced prices, at last beginning to appraise leather belting at its true value. Hitherto, or at least previous to the present scarcity, leather belting was, in a relative sense, sufficiently cheap as a power-transmitting medium to justify some of the lack of care bestowed upon it as a means to prolonging its period of efficient service.

It was not at all an uncommon thing in the past for writers who had ventured an article in the technical Press, advocating strongly the desirability for spending a few hours weekly on the care and maintenance of leather belts, to be told in the correspondence columns of the respective journals that it was a waste of time and money; that all the so-called belt revivers and belt foods, slip preventatives and power augmentors applied to leather belting were all more or less frauds, deleterious to the material, and brought the life's end of a belt appreciably nearer than if

* *The Leather World*, Dec. 12, 1918.

allowed to perform its duties in a natural way and without the aid of preservatives.

That this represented a large share of the opinions held by power users cannot be contradicted, for it has been the present writer's fate in bygone days to be thus "skull-dragged" through the columns of some of our technical journals when he had ventured such an article therein.

To-day, however, feeling in this direction has undergone a radical change—a change towards saner thought and more practical reasonableness. And the reason for such a change is not far to seek. The exigencies of the past few years have forced to the front the use of textile belting, on the whole with not the same satisfactory results as obtained under the leather-belting *régime*.

True it may be that several converts to the application of the textile belt have been made, but these would doubtless be found to represent that small minority of power users whose demands are less exacting, or whose conditions are eminently suitable to the employment of other than leather belts.

But among those who are better qualified to judge, whose demands represent the maximum in power-transmission problems as embraced by belt driving, whose range of conditions necessitates the employment of an element at once durable and strong, and capable of resisting to the last degree the most severe exactions that can be imposed—these always have, and doubtless always will, swear by leather belting. And as an engineer with a long and somewhat comprehensive experience in belt-driving problems, I not only am fully persuaded that these views are very widely held, but I subscribe to them myself.

While there is leather to be obtained for belting purposes it will be had, at whatever the cost, by those who can realize what real economy is and what stands for durability and efficient service.

High as the cost of leather belting is to-day, belting one's pulleys with leather is just as much a profitable investment now as heretofore; that is, providing the very best material is selected, and that it be subsequently preserved as nearly as possible in that condition as modern tanning processes made it.

The most fruitful source of injury to leather belts are overloading and subsequent neglect. Many power users expect a

new leather belt to transmit its full power output as soon as put upon the pulleys, forgetful, or perhaps ignorant, of the fact that its maximum strength and efficiency is potential rather than actual, that such a maximum must be reached in progressive stages. A few realize this, and make a practice of subjecting a new belt to nearly its full working tension for a fairly long period previous to applying it to the pulleys, and always with enhanced results.

This may be done either by hanging the belt and attaching to its extremity a heavy weight, or by attaching one end of it to a pillar or a post, and from another support attaching a set of chain blocks which will exert a definite pull or tension on the belt. This method reduces its ultimate elasticity, hardens and toughens the texture, and prevents that tendency, inherent in leather-belting, to stretch unequally, and so give trouble by running drunkenly upon the pulleys.

It is invariably ruinous to a leather belt to so strain it the first time on a pair of pulleys as to compel it to deliver its full load. This maximum is better reached only after it has been running for a time at, if possible, reduced load; then at each progressive stage it will require some shortening until the strain on the working side of the belt attains its normal. This applies more particularly to unstretched belting. By following out the recommendation given above much time would be saved in getting a leather belt into workable trim, and the danger of overloading it in its initial stages would be eliminated.

The life of a leather belt is what you make it. Seeing that leather is a practically indestructible material, that it does not corrode, or oxidize, or ferment, or crystallize, it only requires considerate treatment and a maintenance of its initial supple qualities to make a leather belt your good and faithful servant for a lifetime.

But to expect this from a belt something is expected from its owner. He must remember that as a boy's physical strength is not equal to a grown man's task, neither will a belt live long if overloaded. And that as it is a practical impossibility to prevent the absorption by the air of the natural oils and moisture contained in leather, which quality imparts to it its unequalled flexibility and power to grip the face of the pulley, therefore must

these be replaced in the same proportion by artificial means. The use of a good belt-dressing of proved value as an effective replacement is therefore highly desirable.

Given these provisions, and leather belting to-day, despite its high cost, is even yet an economic proposition.

CORRECTIONS TO TENTATIVE STANDARD METHODS FOR THE SAMPLING AND ANALYSIS OF COMMERCIAL FATS AND OILS.[1]

SAMPLING[2].

Sampling from Car on Track.—(b) When Contents are Liquid.

Add to this paragraph the following sentence: "In place of the device described above, any sampler capable of taking a sample from the top, bottom, and center, or from a section through car, may be used."

ANALYSIS.

Soluble Mineral Matter.

In the sentence reading "Ash the residue in a muffle, to constant weight, taking care that the decomposition of carbonates is complete, etc.," insert the words "alkaline earth" before the word "carbonate."

Unsaponifiable Matter.

Under *Determination* strike out the last sentence reading, "When the unsaponifiable matter runs over 5 per cent., etc." Add immediately after the sentence which now reads, "Repeat extraction at least four more times, using 50 cc. petroleum ether each time," the following: "More extractions than five are necessary where the unsaponifiable matter runs high, say over 5 per cent., and also in some cases where it is lower than 5 per cent., but is extracted with difficulty."

Wijs Method for the Determination of Iodine Value.

Change heading to read *Iodine Number—Wijs Method.*

[1] Methods of American Chemical Society, *J. I. and E. C.*, pp. 69-71 Jan., 1919.

[2] See this JOURNAL, p. 14, Jan., 1918.

Under *Preparation of Reagents—Wijs Iodine Solution*—(2). The sentence "Or dissolve 6.5 g. of resublimed iodine," should read "13 g. of resublimed iodine."

Add under *Preparation of Reagents—Wijs Iodine Solution*, a third paragraph, reading as follows: "There shall be no more than a slight excess of iodine, and no excess of chlorine. When the solution is made from iodine and chlorine, this point can be ascertained by not quite doubling the titration."

METHODS OF ANALYSIS ADOPTED SEPTEMBER 4, 1918.

Melting Point.

Apparatus.—Capillary tubes made from 5 mm. inside diameter thin-walled glass tubing drawn out to 1 mm. inside diameter. Length of capillary part of tubes to be about 5 cm. Length of tube over all 8 cm.

Standard thermometer graduated in tenths of a degree.

600 cc. beaker.

Determination.—The sample should be clear when melted and entirely free from moisture, or incorrect results will be obtained.

Melt and thoroughly mix the sample. Dip three of the capillary tubes above described in the oil so that the fat in the tube stands about 1 cm. in height. Now fuse the capillary end carefully by means of a small blast flame and allow to cool. These tubes are placed in a refrigerator over night at a temperature of from 40 to 50° F. They are then fastened by means of a rubber band or other suitable means to the bulb of a thermometer graduated in tenths of a degree. The thermometer is suspended in a beaker of water (which is agitated by air or other suitable means) so that the bottom of the bulb of the thermometer is immersed to a depth of about 3 cm. The temperature of the water is increased gradually at the rate of about 1° per minute.

The point at which the sample becomes opalescent is first noted and the heating continued until the contents of the tube becomes uniformly transparent. The latter temperature is reported as the melting point.

Before finally melting to a perfectly clear fluid, the sample becomes opalescent and usually appears clear at the top, bottom, and sides before becoming clear at the center. The heating is continued until the contents of the tube become uniformly clear

and transparent. This temperature is reported as the melting point. It is usually only a fraction of a degree above the opalescent point noted. The thermometer should be read to the nearest ½° C., and in addition this temperature may be reported to the nearest degree Fahrenheit if desired.

Cloud Test

Precautions.—(1) The oil must be perfectly dry, because the presence of moisture will produce a turbidity before the clouding point is reached.

(2) The oil must be heated to 150° C., over a free flame, immediately before making the test.

(3) There must not be too much discrepancy between the temperature of the bath and the clouding point of the oil. An oil that will cloud at the temperature of hydrant water should be tested in a bath of that temperature. An oil that will cloud in a mixture of ice and water should be tested in such a bath. An oil that will not cloud in a bath of ice and water must be tested in a bath of salt, ice, and water.

Determination.—The oil is heated in a porcelain casserole over a free flame to 150° C., stirring with the thermometer. As soon as it can be done with safety, the oil is transferred to a 4 oz. oil bottle, which must be perfectly dry. One and one-half ounces of the oil are sufficient for the test. A dry Fahrenheit thermometer is placed in the oil, and the bottle is then cooled by immersion in a suitable bath. The oil is constantly stirred with the thermometer, taking care not to remove the thermometer from the oil at any time during the test, so as to avoid stirring air bubbles into the oil. The bottle is frequently removed from the bath for a few minutes. The oil must not be allowed to chill on the sides and bottom of the bottle. This is effected by constant and vigorous stirring with the thermometer. As soon as the first permanent cloud shows in the body of the oil, the temperature at which this cloud occurs is noted.

With care, results concordant to within ½° C. can be obtained by this method. A Fahrenheit thermometer is sometimes used because it has become customary to report results in degrees Fahrenheit.

The oil must be tested within a short time after heating to

150° C. and a re-test must always be preceded by reheating to that temperature. The cloud point should be approached as quickly as possible, yet not so fast that the oil is frozen on the sides or bottom of the bottle before the cloud test is reached.

Notes on the Above Methods.

Melting Point.

A melting point is the temperature at which a solid substance assumes the liquid condition. If the solid is a pure substance in the crystalline condition the melting point is sharp and well defined for any given pressure. With increased pressure the melting point is lowered or raised, depending on whether the substance contracts or expands in melting. The lowering or raising of the melting point with pressure is very slight and ordinarily is not taken into consideration. Melting point determinations are commonly carried out under ordinary atmospheric pressures without correction. The general effect of soluble impurities is to lower the melting point, and this holds true whether the impurity has a higher or lower melting point than the pure substance (solvent). Thus if a small amount of stearic acid be added to liquid palmitic acid and the solution frozen, the melting point of this solid will be lower than that of palmitic acid. Likewise the melting point of stearic acid is lowered by the addition of a small amount of palmitic acid. A eutectic mixture results when two components solidify simultaneously at a definite temperature. Such a mixture has a constant melting point and because of this and also because both solid and liquid phases have the same composition, eutectic mixtures were formerly looked upon as compounds. The phenomenon of double melting points has been observed in the case of a number of glycerides. Such a glyceride when placed in the usual capillary tube and subjected to increasing temperature quickly resolidifies only to melt again and remain melted at a still higher temperature. This phenomenon has not yet been sufficiently investigated to afford a satisfactory explanation.

Non-crystalline substances such as glass, sealing wax and various other waxes and wax mixtures, and most colloidal substances do not exhibit a sharp melting point but under the application

of heat first soften very gradually and at a considerably higher temperature melt sufficiently to flow. This phenomenon of melting through a long range of temperature may be due to the amorphous nature of the substance or to the fact that it consists of a very large number of components of many different melting points.

The fats and oils of natural origin, that is, the animal and vegetable fats and oils, consist of mixtures of glycerides and, generally speaking, of a considerable number of such components. These components are crystalline and when separated in the pure state have definite melting points, although some exhibit the phenomenon of double melting point. For the most part the naturally occurring glycerides are mixed glycerides. In the natural fats and oils there are present also certain higher alcohols of which cholesterol is characteristic of the animal fats and oils and phytosterol of many of the vegetable fats and oils. In addition to the crystalline gylcerides and the higher alcohols present in neutral fats, there are in fats of lower grade, fatty acids, which are crystalline, and also various non-crystalline impurities of an unsaponifiable nature, and the presence of these impurities tends to lower the melting point. They also tend to induce undercooling when the liquid fat or oil is being chilled for purposes of solidification or in determinination of titer.

The presence of water, especially when this is thoroughly mixed or emulsified with a fat or oil, also influences the melting point to a marked extent, causing the mixture to melt through a longer range of temperatures than would be the case if the water were absent. This is particularly true of emulsified fats and oils, such as butter and oleomargarine, both of which contain, besides water, the solids naturally present in milk or cream and including casein, milk sugar, and salts. The melting point method recommended by the Committee is not applicable to such emulsions or other watery mixtures and the Committee has found it impossible to devise an accurate method for making softening-point or melting-point determinations on products of this nature. Not only the amount of water present but also the fineness of its particles, that is, its state of subdivision and distribution, in a fat or oil influences the softening point or melting point and causes it to vary widely in different samples.

As a consequence of the foregoing facts, natural fats and oils do not exhibit a definite melting point, composed as they are of mixtures of various crystalline gylcerides, higher alcohols, fatty acids, and non-crystalline substances. Therefore, the term melting point when applied to them requires further definition. Various methods have been devised to determine the so-called melting point of fats and oils. Most of these methods, however, determine, not the melting point, but the softening point or the flow point of the fat and the great difficulty has been in the past to devise a method which would determine even this point with reasonable accuracy and so that results could be easily duplicated. It has been the aim of the Committee to devise a simple method for the determination of the melting point of fats and oils, but it should be understood that the term melting point in the scientific sense is not applicable to natural fats and oils.

Bichromate Solution.

The Committee calls attention to the fact that occasionally potassium bichromate is found containing sodium bichromate, although this is of rare occurrence. If the operator suspects that he is dealing with an impure potassium bichromate, the purity can be ascertained by titration against re-sublimed iodine. However, this is unnecessary in the great majority of cases.

Glacial Acetic Acid.

The glacial acetic acid used for preparation of the Wijs solution should be of 99.5 per cent. strength or higher and should have a freezing point of 14.7 to 15° C. (m. p. 16.7°). In case of glacial acetic acids of somewhat lower strength, the Committee recommends freezing and centrifuging or draining as a means of purification.

ABSTRACTS.

The Tilston-Melbourne and the Forsare Liming Processes. In two recent issues of *The Leather Trades Review* (Nov. 13 and Dec. 11, 1918) are given descriptions of two patented methods of rapid liming. Two different tanneries where these processes were installed were visited by a reporter for this paper and he makes the following notes. The Tilston-Melbourne process depends upon the mechanical stirring of the lime by a

paddle while in the Forsare process the lime is agitated by compressed air.

In the Tilston-Melbourne patent the whole hides are suspended in specially constructed vats by the neck and tail along the back, the hair side being out. The hides are not given a preliminary soaking but are hung in the limes directly from the hide cellar. The vats are similar in shape to those commonly in use, except that the bottom is made concave to assist in the upward movement of the lime by the paddle. At the bottom of the vat is a paddle, running the length of the vat, and in an opposite direction to the line in which the hides are hung. These paddles are operated in pairs by rods and arms from an eccentric on an overhead shaft. The practice is to give the hides two limes. They are first placed in a vat from which a finished pack of 50 hides has been taken. They are kept in this lime two days, the paddle being run for five hours daily. This movement of the paddle besides stirring up the lime, causes the hides to bellow slightly, thus reducing the tendency of the flesh sides to cling together. At the end of two days the old lime is run off, the vat is filled with water, and 3½ pounds of lime with a little sodium sulphide (mixed together as a paste) is added. The hides are kept in this lime three days more with five hours paddling daily, after which the hides are unhaired.

The advantages of this process are manifold. The hides can be examined and tested at any stage of the process. There is no danger of lime stains. There is less loss of hide substance. The vats can be easily emptied and cleaned as the contents are always fluid. There is no damage to the grain by hook marks. But the most important are the economies in labor, material, and time. Besides all these the hides are uniformly penetrated and plumped, the grain is perfectly firm and the hair comes off easily and evenly.

The Forsare process, sometimes called the Walker-Bolton process, depends for its agitating action on compressed air. The whole hides are hung in vats either on slats or by hooks along the back line with the hair out, and water run on. Then the water is agitated vigorously for a short time by air blown in from tubes across the bottom of the vat. This washes the hides free of manure, dirt, etc. This water is then blown out by an air lift. The vat is then filled with a used lime liquor, or with clean water and milk of lime with some sodium sulphide is added. The air is turned on, and the liquor kept in agitation continuously for three or four days. Lime may be added from time to time as necessary. The hides are then ready for unhairing.

The advantages claimed for this process are the same as for the Tilston-Melbourne process. One addition, however, is the lack of costly agitating machinery and the ability to put the air lines in any part of the plant in a very short time and at little expense. One central compressor can be used with lines radiating wherever needed. The air pressure required is from 12 to 15 pounds above atmospheric pressure, and this would require about 15 h.p. to deal with 1,000 heavy hides weekly. The inventors are at present working on a scheme to hang the hides on port-

able frames which can be lifted bodily from the lime vats and carried by an overhead railroad wherever wanted. W. A. F.

The Influence of Electrolytes Upon the Osmotic Pressure of Gelatin Solutions. JACQUES LOEB. Rockefeller Inst. *J. Biol. Chem.*, 35, 497-508 (1918); *Chemical Abstracts*, Dec. 10, 1918.—"It is generally stated in colloid chemistry that only acids and bases cause an increase in the swelling, the viscosity, and the osmotic pressure of hydrophylic colloids, while neutral salts of the type of NaCl have little or, according to Lillie, a directly opposite effect. The writer has found that neutral salts act exactly like acids and bases inasmuch as neutral salts and bases with univalent cation and acids with univalent anion increase the swelling, the viscosity, and resistance to pptn. by alc. of gelatin, while salts and bases with bivalent cation and acids with bivalent anion (with the exception of some org. acids) have no or only a slight effect. The same is true for the influence of electrolytes upon the osmotic pressure of gelatin. It was found that only the cation of neutral salts acts upon gelatin in neutral solns. or in solns. with $P_H > 4.7$, while the anion of neutral salts does not influence the osmotic pressure and the other physical qualities of gelatin. These expts. contradict the statements generally made in colloid chemistry that the influence of neueral salts upon a protein is the algebraic sum of the opposite effect of the oppositely charged ions of the neutral salts. They also contradict the statement that common gelatin (at the point of neutrality) is influenced more strongly by the anion than by the cation of a neutral salt. The difference between our results and those of the older experimenters is due to the fact that in the older expts. the effects of neutral salts upon gelatin were always measured in the presence of the salts. The presence of the salts represses the manifestations of its effects upon the gelatin and it is therefore necessary to remove the excess of the salt after it has had time to act on the protein." The results are in accord with the following theory of amphoteric electrolytes: "that on the more acid side of their isoelec. point amphoteric electrolytes can exist, when ionized, only in the form of cations, while on the less acid side of their isoelec. point they can exist, when ionized, only as anions. In the former case the ampholyte can combine only with the anion, in the latter only with the cation of a neutral salt. Since gelatin has its isoelec. point at $P_H = 4.7$, while the gelatin used had a $P_H = 7$, such gelatin could react only with the cation of neutral salts."

Physiological Investigation of a New Yeast Mold from the Tanning Vat. TOICHI ASAI. Rigakushi, Japan. *J. Coll. Sci Imp. Univ. Tokyo*, 39, Art. 7, 42 pp., with micro-photographs (1918); *Chemical Abstracts*, Dec. 10, 1918.—This is not Eitner's *Mimosa-flecken*, for Mimosa bark is not used in the tannery in Senju, near Tokio, in which it is found. *Mycoderma tannica*, nov. sp., forms thick, brown-red patches on sole leather, which consist of the remains of the organism, and is not a chem. stain. Cultivated on gypsum without nutrient at 30° it forms large, thick-

walled resting cells, 7-3-7.9 in. diam., filled with glycogen and fat droplets. It assimilates the hexoses, especially glucose and levulose, but neither maltose, lactose, dextrin, glycogen nor inulin. One per cent. EtOH is as good a nutrient as three per cent. cane sugar. It endures tannin as a sole nutrient only in very dil. soln., but when glucose and asparagine are present also, its activity is four times as great as in the same strengths of these without the tannin. The patches it forms on sole leather are not removable by acids or bleaching agents. When present in the vat, it removes EtOH, AcOH, lactic acid and tannin, and retards the growth and activity of other useful organisms. A list of organisms in the tan vats, and in the air of the tannery is given. *Mycoderma tannica* is found in the air, not in the water, or on the tanning exts.

Galloyl Derivatives of Dextrose; Comparison with Chebulic Acid. E. Fischer and M. Bergmann. *Berichte*, 1918, 298-320; *J.C.S.*, 1918, i. 224-225. Chebulic acid gives gallic acid and dextrose on hydrolysis but does not appear to be related in structure to the galloyl-glucoses. Mono- and tri-galloylglucose were prepared by means of glucosemonoacetone and glucosediacetone (*vide* *J.C.S.*, 1916, i., 363), and were thoroughly compared with chebulic acid. This acid gives dextrose on hydrolysis with N/1 sulphuric acid, but the process is much slower than with tri- and penta-galloylglucose. Methylated chebulic acid differs markedly from methylated tri-galloylglucose. Mono-galloylglucose gives a deep blue with ferric chloride but gives no precipitates with gelatin or bases, nor is it identical with Feist's glucogallic acid (*vide* *J.C.S.*, 1914, i., 989).

Retardation by Sugars of Diffusion of Acids in Gels. E. A. and H. T. Graham. *J. Am. Chem. Soc.*, 40, 1900 (1918).—The experiments described in this paper were undertaken to determine the effect of the presence of sugars upon the rate of diffusion of acids in gelatin jellies. The sugars used were glucose, saccharose, and lactose, which were added to the gelatin solutions in varying amounts along with litmus as indicator; the solutions were then diluted so that 10% was the final concentration of gelatin in each solution, which was then allowed to set in suitable tubes. 0.2N solutions of the following acids were employed: hydrochloric, sulphuric, nitric, phosphoric, lactic, formic, acetic, and butyric. The acid solutions were carefully run onto the tops of the gels and the distance of penetration of the acid into the gel in millimeters, as shown by the line of division between the acid and neutral shades of litmus, was noted at definite intervals. The temperature was kept at 26°.

In every case the presence of sugar in the gel resulted in a marked retardation of the diffusion of all acids tried and the greater the concentration of sugar the greater the retardation. In 144 hours 0.2N HCl penetrated the gel containing no sugar 54 millimeters, the gel made 0.5M with glucose 44 millimeters, and the gel made 0.5M with saccharose only 39 millimeters. The amount of retardation produced by sugars increases with the concentration, but not in direct proportion to it, the retardation

being proportionately greater for the smaller concentrations of sugar. It was found also that the presence of salt in a gel has a measurable effect in retarding the diffusion of acids, but not nearly so marked as that of the sugars.

There seems to be no relation between the degree of retardation and the rate of diffusion of the acid, since phosphoric acid was retarded more than the faster acetic acid. In general the stronger acids were retarded more than the weaker, but this was not invariably the case, since lactic acid was not retarded more than the weaker acetic acid. Since saccharose and lactose produced about the same degree of retardation, it is suggested that all disaccharides have approximately the same retarding power and all monosaccharides equal retarding powers, but smaller than those of the disaccharides. It is hoped to test this point experimentally.

It is mentioned that with sugar the retardation of diffusion may be due in part to some chemical action between the acid and sugar, or possibly to the increased viscosity of the gel. But neither of these possibilities would account for the retardation by salt, since there could be no chemical action between HCl and NaCl, and the addition of salt to a gelatin gel actually lowers the viscosity and would therefore tend to increase diffusion.

A comparison is made between this retarding influence of salt and sugars and the power of these substances to repress the swelling of gelatin plates which are immersed in acid solutions. Salt retards the diffusion of acids in gels much less than the sugars, but it has a more powerful effect in repressing the swelling of acid-swollen gelatin. In this connection the works of Procter and of Fischer are mentioned. (Abstractor's Note: It may be well to remind the reader that Procter dealt primarily with systems which had reached a state of equilibrium; the present paper deals with changes in systems approaching equilibrium, but not at all with the conditions obtaining at equilibrium. Another fundamental difference, which the authors point out, is that in the swelling experiments the salt or sugar was originally placed in the external solution, whereas in the diffusion experiments it was placed in the gel. Procter's object in starting with a consideration of systems already in a state of equilibrium was to render as simple as possible an extremely involved problem in the hope that the solution of the simplest case might serve as a foundation and stepping stone to the more complex considerations of systems in a continual state of change. It is probable that in the majority of operations in the tannery equilibrium is never reached and that the molecular mechanism of these actions is so complicated as to be impossible of mental picturing, except in the form of equations of higher mathematics. Procter has already given equations which explain quantitatively conditions obtaining at equilibrium and at least qualitatively many conditions while the systems are in a state of change. The present paper is deserving of the attention of the leather chemist, because, like others dealing with the properties of gels and solutions, it adds its mite to our knowledge of systems obtaining in the tannery. The greater our

knowledge of such things the better are we prepared by pure reasoning to increase our efficiency in making leather.)

The paper contains 4 figures and 8 tables of experimental data.

J. A. W.

New Methods of Tannin Estimation and Their Practical Value as Compared with the Hide Powder Process. R. LAUFFMANN. *Coll.*, 1918, 185-190; *J. S. L. T. C.*, Dec., 1918.—A critical review of various processes suggested since Dekker published his book on "The Tannins," 1913. Zwick (*Coll.*, 1908, 281) made observations on the refractive power of solutions of tans and non-tans for different materials and suggested that the figures obtained should be used to estimate the tannin content of a liquor from its refractive index before and after being detannized. These equivalent figures are influenced by the mode and temperature of leaching, they also vary considerably with the same material and are entirely useless for the estimation of tannin in mixed liquors.

Vanicek (*Coll.*, 1909, 146) based a process on the supposition that all tannins consist of tannic acid and neutral matter in a definite constant proportion, and thus he proposed to estimate the tannin content from the difference in alkali required for original and detannized solutions. His assumption of a definite constant proportion is inadmissible since the acid content of tannin solutions alters on standing and even the tannins themselves separate out. Like all titration methods it is also inaccurate owing to the difficulty in observing the end point especially with catechol tans.

Eglen's process (*Le Cuir*, 1914, 18) based on the assumption of a constant relationship between the total solubles and the tannin content of liquors derived from one and the same material is open to the same objections. The relationship is not constant and Eglen's proposal to detannize with gelatine seems open to question.

Gawalowski (*Ledertech. Rundschau*, 1915, 337) has modified his method of tannin estimation with basic copper acetate. The extract or material is treated with a mixture of 2 parts ether and 1 part alcohol, an aliquot portion of the solution is evaporated at 40° C, the residue dissolved in water and the solution precipitated with basic copper acetate. The alcohol ether extraction obviates the presence of resins and pectins in the tannin solution as otherwise these would be precipitated along with the tannins. The copper tannate is washed, dried, weighed, ashed, reduced to copper and weighed again. The tannin is given by the difference in the two weights. It seems doubtful whether the alcohol-ether treatment is effective in its aim, also some insoluble tans are counted as non-tans. A further source of error occurs in the decomposition which takes place during the washing of the copper tannate.

Levi and Orthmann (*Coll.*, 1913, 525) have precipitated tannins with solutions of a chromium compound and determined certain factors for the tannin value of the precipitate. These, like other factors, are not constant, however.

Kohn-Abrest (*J.A.L.C.A.*, 1914, 260) and Singh and Ghose (*J.A.L.C.A.*, 1916, 181-185) recommend the adoption of inorganic adsorbents for detannizing the solutions. These methods seem very arbitrary since the adsorbent material is entirely different to hide powder. Errors in the hide powder process are often traceable to fermentation of the liquors or unsuitable treatment of the samples. The great superiority of the hide powder process consists in that no materials are used either physical or chemical which are not present in the tannery.

Influence of Iron and Organic Matter on the Iodometric Estimation of Chromium. R. LAUFFMANN. *Coll.*, 1918, 223-228; *J.S.L.T.C.*, Dec., 1918.—A series of experiments suggested by the work of Schorlemmer, Lamb and Harvey. The influence of both iron and organic matter was determined by iodometrically estimating the chromium in:—

(1) A solution of chromium sulphate after oxidation with sodium peroxide and also fusion mixture.

(2) The same chrome liquor with the addition of ferric chloride:
   (*a*) Dissolving ferric hydroxide after oxidation with peroxide in excess hydrochloric acid.
   (*b*) Ferric hydroxide removed by filtering off.

(3) Same chrome liquor with addition of cane sugar, glucose, starch and soluble proteins.

TABLE.

	Grs. Cr_2O_3 found in 100 cc. solution	
	Peroxide oxidation	Oxidized with fusion mixture
Pure chromium sulphate..............	0.0970	0.0970
Chromium sulphate and ferric chloride .	(*a*) 0.1025	
	(*b*) 0.0932	
	(*c*) 0.0960	
Chromium sulphate and organic matter.	After standing	
	½ hour 0.0825	
	24 hours 0.0890	
	60 hours 0.0960	

Using the iodometric method of chromium estimation after oxidation with sodium peroxide the results come out too high in presence of appreciable amounts of iron, owing to the separation of more iodine. Where the ferric hydroxide is filtered off, a low chromium content results from the precipitate retaining some adsorbed chromate solution. If large amounts of hydroxide precipitates separate out after oxidizing the chromium with sodium peroxide too low results are obtained on filtering since the precipitates absorb some chromate and even careful treatment with water does not wash it out. If these precipitates are bases which do not separate iodine from potassium iodide, and their hydroxides are soluble in acid there is no need to filter but the precipi-

tate should be dissolved up and the chromate estimated in the solution. Large amounts of organic matter in a chromium solution give rise to inaccurate results by the peroxide oxidation method since they retard the separation of the iodine and render the end point indistinct.

Venezuelan Production of Balata. *J.R.S.A.,* Dec. 6, 1918.—Balata, a gum similar to gutta-percha is largely used in the manufacture of belting. It is obtained from the sap of *Mimusops globosa,* a tree reaching a height of 100 feet or more, which is widely distributed over eastern Venezuela and the Guianas. The latex is secreted between the bark and the wood of the tree; it contains nearly equal proportions of resin and gutta, the latter being identical with true gutta-percha. The word balata is applied only to the gum, the tree being known as the purguo. In some places the tree is called the nisperillo. The average production of the gum per tree is 18 pounds, with a value of from 15¢ to 40¢ per pound.

In Venezuela, the custom is to cut down the tree in order to obtain the sap, the industry thus progressively destroying itself. In the Guianas felling is prohibited and the latex is obtained by regular tappings that do not kill the trees. The tree is very slow in growth, it requiring thirty or more years for the full development of the productive stage. Natural reproduction is slow and as a consequence the available supply of balata is gradually failing. In 1911 over $2,400,000 worth of the gum was exported, while in 1915 less than $800,000 worth was produced. The war has changed the course of the trade in the gum and while the most of it used to go to Germany, it now goes to England and the United States.

W. A. F.

Theory of Leather Formation, V. W. Fahrion. Coll., 1918, 173-178, 213-14; *J. S. L. T. C.,* Dec., 1918.—In reply to Moeller's criticism that the chemical theory of tanning was largely based on the assertion that free amino acids are precipitated by formaldehyde, the author points out that this is a gross mis-statement and that Abt and Stiasny (*Coll.* 1910, 189) only stated that free amino acids could be titrated with formaldehyde. Chemists have hitherto made great distinction between adsorption compounds and solid solutions. Oryng (*Koll. Zeit.* 1918, 22, 149) says all adsorption compounds are being proved to be chemical compounds. If such a view prevails then the discussion between chemical and physical tanning theories will happily vanish.

Moeller's analogy between the behavior of formaldehyde with albumens and with collagen is false since collagen is not an albumen but an albumenoid. That acetaldehyde tans very little and aromatic aldehydes scarcely at all, does not confound the chemical theory of tanning but merely shows that not only is aldehydic oxygen necessary for tanning but also a methylene group directly united to that oxygen. With reference to hide powder not taking up acid after treatment with formaldehyde, Stiasny first resorted to Moeller's membrane formation theory but abandoned it because formaldehyde is not adsorbed by animal charcoal.

Water is necessary for the formation of methylene glycol, the peptizer of Moeller's theory but formaldehyde can tan in alcoholic solution. It is incorrect to say that the small amount of formaldehyde is stoichiometrically insufficient to react with the collagen. The action of the polymerization products can be easily explained by catalysis without Moeller's peptization theory.

Moeller lays great emphasis on his experiment with o-nitrobenzaldehyde and acetone but it would be very difficult to completely free the pelt from uncombined aldol by washing. Besides these are reversible chemical combinations so that the possibility of the aldol being given up again is not precluded. Even the polymers of formaldehyde are chemical compounds and such an addition compound can be assumed in the case of the collagen acetone system so that the chemical theory completely explains Moeller's observations by a question of difference of affinity.

The discussion finally resolves itself into explaining the resistibility of aldehyde leather to hot water. Physical theorists attribute it to a formaldehyde polymer membrane round the hide fibres which is impermeable to hot water. With regard to the quinone tannage, Moeller's numerous experiments do not offer convincing proofs. By rubbing together 1.5 grs. hide powder with 0.5 grs. quinone in a mortar the characteristic quinone tannage colorations were obtained, and after leaving in contact for two days, extracting with warm alcohol and drying, a product was obtained which gave the high water resistibility figure 92.1. This shows that the decomposition products given by quinone with water are unnecessary for tanning and further it leads to the conclusion that Moeller's peptization theory is superfluous and incorrect.

Proposed Electric Tanning in Dublin.—The vice-consul at Dublin reports that an application has been made to the Corporation of Dublin by the "Irish Tanning Corporation" now in process of formation for a site at the North Wall for the purpose of installing plant and erecting works to carry out the system of tanning by electricity.

For this process many advantages are claimed over the older methods, and it is stated that is intended to establish in Dublin an up-to-date tannery upon the most modern principles. L. M. W.

Rapid Method of Butter Analysis. E. F. KOHMAN. *J. I. and E. C.*, p. 36, XI, 1919.—Inasmuch as a fat standard for butter is advocated by many, it would be desirable to have some simple and rapid method for the determination of fat in butter to be used in creamery control work. The author found that with very little added time the fat can be determined in connection with the moisture test in the following manner:

The moisture is determined as usual over a small flame in a tall, rather narrow, lipped aluminum beaker with a capacity of about 100 cc., using a 10 g. sample. After the beaker is weighed to determine the loss of moisture, it is filled with petroleum ether and the contents stirred with a glass rod to secure a thorough mixture. It is then covered with

a watch crystal and allowed to stand 2 or 3 min. for the mixture of curd and salt to settle, when the solvent is gently decanted off without disturbing the sediment. The beaker is then filled with fresh solvent. The curd and salt mixture settles rapidly in the fresh solvent and the liquid can be decanted off after a very short time. By gently heating the beaker now, either on a water bath, a hot plate, or directly over a small flame, but not so rapidly as to cause sputtering, the sediment can be completely freed of petroleum ether by evaporation in a very short time. The per cent. of fat is then determined by difference upon re-weighing the beaker with its contents. The salt is now in ideal condition to be determined by titration, using a solution of such strength that the number of cc. used represents the per cent. of salt.

No special practice is necessary in order to enable one to carry out this analysis successfully the first time. The author had no difficulty in assigning it to his students in dairy chemistry. In heating the butter to drive off the moisture, the slightest noticeable browning of the sample should be taken as the end-point. But it is surprising how little the results are affected if the sample is heated until it assumes a coffee-brown. Before trying to evaporate the petroleum ether from the mixture of curd and salt, it is well to loosen it from the bottom of the beaker by gently tapping it on the desk in order to lessen the tendency to sputter. When making duplicate determinations the two beakers can readily be held by one pair of tongs while being heated. The author has been able to make duplicate analyses of butter in 20 min. or single determinations in 15 min., and the results are as accurate as those obtained by the A. O. A. C. methods. It is well to keep the petroleum ether from the second decantation in a separate container and use it for the first extraction in future analyses.

fulling mill to the action of glue or gelatin and a little nitric acid. For upper leathers and chrome retanned leathers a vegetable oil such as castor or linseed is added.

Leather Substitute. British Patent 119,304. J. WARD, Bedford, England. Coarse felt impregnated and filled with leather powder, vulcanized rubber powder, and free sulphur, heated to a semi-liquid state. To this may be added resin, sodium silicate and coloring matter.

Leather Substitute. British Patent 119,902. J. L. WATKINS, London. England. A rubber substitute made up of scrap and new rubber, and a cotton or other vegetable fiber, and includes Kapok. Asbestos, jute fiber, silk fiber, a metallic oxide, a vulcanizing agent, crushed slate, cement and a coloring matter may be added.

Tanning. British Patent 120,049. C. BLANC, Paris, France. Chromic liquors are made by reducing chromic acid by cellulose or lignocellulose materials. The cellulose materials may be sawdust, cotton, straw, paper waste, wood fibers, brewery residues, olive husks oil free, etc.

Leather Compositions. British Patent 120,802. H. E. WHITE, Birmingham, England. Leather scrap is first treated with weak acid, such as 10 per cent. hydrochloride. Salts such as magnesium sulphate or sodium chloride may be added. The excess of acid is removed and the mass heated. Alcohol, olive oil, or gelatine may be added while heating. The mass is then hardened with formaldehyde, chrome liquor or vegetable tannins, or by picric acid. Organic or inorganic filling materials may be added.

Tanning Bate. British Patent 120,928. L. R. PEYRACHE, Paris, France. A powder made from fresh pancreatic glands of animals to which may be added deliming agents.

Bating Hides and Skins. German Patent 305,898. E. LUKSCH, Vienna. The waste liquors obtained in the manufacture of tartaric acid, after precipitating out the calcium tartrate make an excellent bating and delimining liquor.

Tanning with Chrome Liquors. German Patent 306,015. E. KANET, Agram. Strongly basic chrome solutions which deposit chromium hydioxide at ordinary temperature can be used when cooled. In some cases it is advantageous to warm the hides after they are completely penetrated by the liquor.

Tanning Agent. Swiss Patent 78,282. Made by sulphonating tar oil and treating it with formaldehyde.

Tanning with Aluminium Salts. Swiss Patent 77,935. O. RÖHM. The formate or acetate is used or the usual alum process followed by the formate or acetate of an alkali or alkaline earth.

Journal of the

American Leather Chemists Association

Vol. XIV | APRIL, 1919 | No. 4

W. K. ALSOP . . . . Editor and Manager
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Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $6.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized July 16, 1918.

CHANGE OF ADDRESS.

Oskar Riethof, 16 Sachem St., Lynn, Mass.

SIXTEENTH ANNUAL MEETING.

The sixteenth annual meeting of the A. L. C. A. will be held at the Marlborough-Blenheim, Atlantic City, N. J., May 22, 23, and 24. An extensive program has been arranged and all members are urged to be present.

The management of the Marlborough-Blenheim suggest that each member communicate with them direct as to their special requirements, so that they may arrange for each one individually.

Following is a schedule of their rates:

	American plan	European plan
Single rooms without bath (per day)	$7, $8	$4, $5
Single rooms with bath (per day)	$10, $11	$7, $8
Double rooms without bath (two persons)	$12	$7
Double rooms with bath (two persons)	$14, $15	$9, $10
Double rooms with bath (ocean frontage)	$18–$21	$13–$16

THE EFFECT OF GREASE ON THE TENSILE STRENGTH OF STRAP AND HARNESS LEATHERS.

By L. M. Whitmore, R. W. Hart and A. J. Beck.[1]

When considering specifications for army leather, it seemed advisable to determine, if possible, the effect of the different constituents on the desirable qualities of the leather. In the case of strap and harness leathers, the prime requisite is tensile strength, and the amount of stuffing to be used is rather important. Another point to be considered was the amount of mineral oils and greases to be permitted. The following experiments were carried out to determine the effect of grease on the tensile strength, and the relative effects of different stuffing mixtures. Stuffing has great value as a waterproofing which is not considered here.

In order to overcome the results of variations in the leather, even where the test strips are cut from single backs, it is necessary to make large numbers of tests, and use averages for comparison. The Bureau had on hand many samples of strap and harness leather, and it was decided to use this material for the tests. Fifty-two different tannages were used and a total of 891 tests made. Any piece large enough to give two strips for tensile strength tests gave a single comparison. A third strip from the same piece gave another comparison, as the two outside strips could each be compared with the central one. In all cases the results given are the averages of tests on strips cut parallel to and adjacent to the strips with which they are compared.

[1] Published with the permission of the Director of the Bureau of Standards.

The test pieces were cut with a ½-inch die, and the thickness measured to 0.01 inch. The figures for tensile strength are given in pounds per square inch cross section. The figures for elongation were obtained by marking a 2-inch section in the center of the test strip, and keeping caliper points opposite the marks as the strip was put under tension. The maximum elongation of this 2-inch strip could then be measured. The strips listed as being restuffed were degreased with petroleum ether and afterwards stuffed with the stated material at a temperature about 10° above the melting point of the stuffing mixture. The percentage of grease in the strips tested was obtained by clipping a small piece from each of the test pieces after the tests were made, and then analyzing the composite sample thus formed. Tensile strength data were obtained on all the tests reported, but it was not possible to get data on the elongation of all the samples. The results on elongation are, therefore, sometimes secured from fewer data than the tensile strength results.

The data obtained are tabulated in the following tables:

TABLE I.

184 Samples tested. Degreased samples compared with those as received from tannery. Average grease content of normal samples, 13.7 per cent.

	As received	Degreased
Average tensile strength	4,631	4,035
Relative tensile strength	114.8	100
Average percentage elongation	35.8	24.4
Relative elongation	146.7	100

TABLE II.

62 Samples tested. Degreased samples compared with samples degreased and restuffed with a petrolatum-paraffin mixture melting at 42° C. Average grease content of restuffed samples, 28.0 per cent.

	Degreased	Restuffed
Average tensile strength	3,890	4,650
Relative tensile strength	100	119.5
Average percentage elongation	24.7	36.9
Relative elongation	100	149.4

TABLE III.

42 Samples tested. Degreased samples compared with samples restuffed with tallow (melting point, 40° C.). Average grease content of restuffed pieces, 28.0 per cent.

	Degreased	Restuffed
Average tensile strength	4,225	4,580
Relative tensile strength	100	108.4
Average percentage elongation	23.6	38.7
Relative elongation	100	164.0

TABLE IV.

43 Samples tested. Degreased strips compared with those restuffed with a mixture of 30 tallow, 30 cod oil, and 20 wool grease. Average percentage of grease in restuffed samples, 26.2 per cent.

	Degreased	Restuffed
Average tensile strength	3,518	4,219
Relative tensile strength	100	119.9
Average percentage elongation	25.2	38.2
Relative elongation	100	151.5

TABLE V.

36 Samples tested. Degreased samples compared with those degreased and restuffed with a mixture of petrolatum, rosin, and mineral oil. Average grease content of restuffed strips, 21.4 per cent.

	Degreased	Restuffed
Average tensile strength	4,456	5,075
Relative tensile strength	100	113.9
Average percentage elongation	31.1	35.1
Relative elongation	100	112.8

TABLE VI.

39 Samples tested. Degreased samples compared with those restuffed with petrolatum in 20 cases, and with a mixture of petrolatum, rosin, and mineral oil in 19 cases. Average grease content of restuffed strips, 23.7 per cent.

	Degreased	Restuffed
Average tensile strength	3,669	4,206
Relative tensile strength	100	114.6
Average percentage elongation	23.9	31.0
Relative elongation	100	129.7

TABLE VII.

The tests tabulated below were each made from a single block of leather, alternate strips being taken for treatment with petrolatum.

	Leather as received				With further stuffing of Petrolatum				
Test	Number of Strips tested	Grease content	Tensile strength	Percentage elongation	Grease content	Tensile strength	Percentage elongation	Percentage increase in tensile strength due to extra stuffing	Percentage increase in elongation due to extra stuffing
A	38	3.4	4,021	29.0	29.8	4,139	33.3	2.9	14.8
B	38	3.6	3,220	33.6	32.1	3,344	41.2	3.9	22.6
C	46	4.5	2,627	90.1	30.3	2,726	45.5	3.8	13.4
D	32	5.9	2,496	48.0	29.5	2,768	51.8	10.9	7.9
E	32	8.3	4,622	25.9	29.7	4,739	27.8	2.5	7.1
F	46	10.3	3,771	23.9	30.7	4,057	26.5	7.6	10.9
G	34	17.8	5,577	27.2	30.6	5,629	33.2	0.9	22.0
H	40	19.5	3,182	26.4	30.2	3,200	28.2	0.6	6.8

It is evident from the above data that there is a decided increase in tensile strength due to the presence of grease. This can be accounted for in two ways.

First: By the fact that proper lubrication allows the fibers to slip over one another and to distribute the strain better through the whole strip. This effect would be influenced by the amount of grease present up to a point where perfect lubrication could be secured, and by the viscosity of the stuffing mixture.

Second: By the strengthening of the fibers themselves. This would result from a minimum amount of grease, and the quantitative effect would depend upon its nature.

That the lubrication effect is actually present, is shown by the illustration. The breaks show that the fibers of the stuffed strips slip over each other, giving the break a frayed appearance as compared with the sharp break of the degreased strips. The second effect may or may not be present, but the net effect is probably a combination of the two.

The normal samples, containing 13.7 per cent. stuffing showed up about as well as the restuffed ones containing twice as much. It is probable that the lower amount is sufficient to give perfect lubrication and the maximum tensile strength, as Table VII shows no appreciable increase in tensile strength with the addition of

grease in cases where the sample contained over 14 per cent. in the first place.

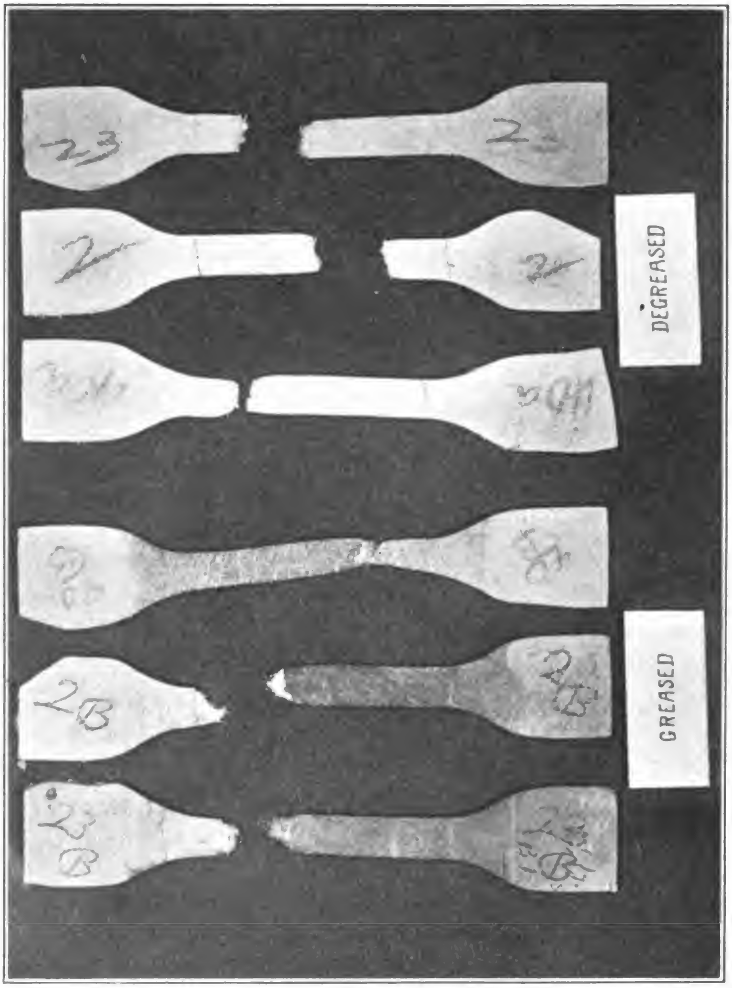


Table VII also shows that the amount of grease necessary to give the maximum tensile strength varies widely, and probably depends not only on the nature of the grease, but on the tannage and the distribution of the grease through the leather.

The relative increase in elongation is much greater than that of tensile strength, and the illustration shows that the cross-section of the heavily greased pieces was greatly diminished by the strain, while that of the degreased ones was not visibly affected.

The statement is frequently heard that only oils of animal origin give strength to the leather. The above data do not seem to bear this out, as the two highest percentage increases in tensile strength were secured with a petrolatum-paraffin stuffing in one case, and with a mixture of cod oil, tallow and wool grease in the other. These results are not intended to show quantitative effect of the different stuffing mixtures used. Quantitative data are more difficult to obtain, but some tests have been started which it is hoped will give some definite relations between the amount of grease necessary to give the maximum tensile strength and the nature of the grease, as well as the relative effects of the different stuffing mixtures.

AN EXTRACTOR FOR WATER-SOLUBLE IN LEATHER.

By H. C. Reed and J. B. Churchill.

The apparatus described below was designed by H. C. Reed to meet an emergency calling for an extractor capable of extracting a number of leathers simultaneously, at a time when owing to conditions it was impossible to secure an apparatus of the standard type without great delay. For the same reason an exact duplicate was made and installed in the American Leather Research Laboratory. At that time the apparatus was looked on merely as a substitute to care for the work until an extractor of the standard type could be secured. The results obtained, however, were so satisfactory and the apparatus so convenient to use that in both of these laboratories it has been permanently adopted for the determination of the water soluble in leather.

The authors make no claim whatever for any originality in the design of the apparatus and it is at the request of several leather chemists who have seen this apparatus and the results obtained that the following brief description is given.

The apparatus consists essentially of a set of twelve glass tubes placed in a large cylindrical (tin-lined) copper container about

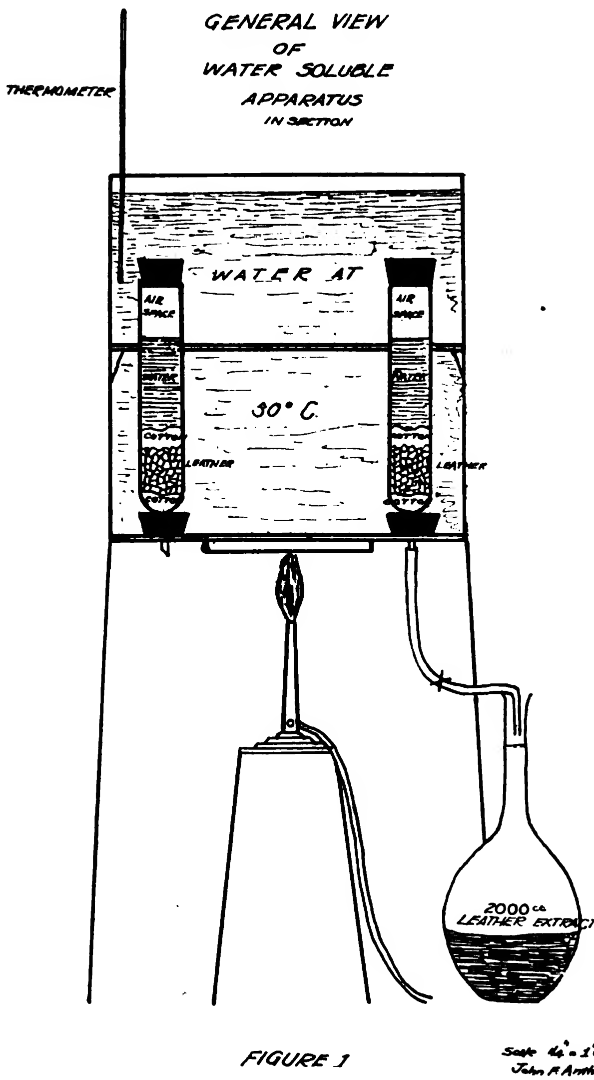
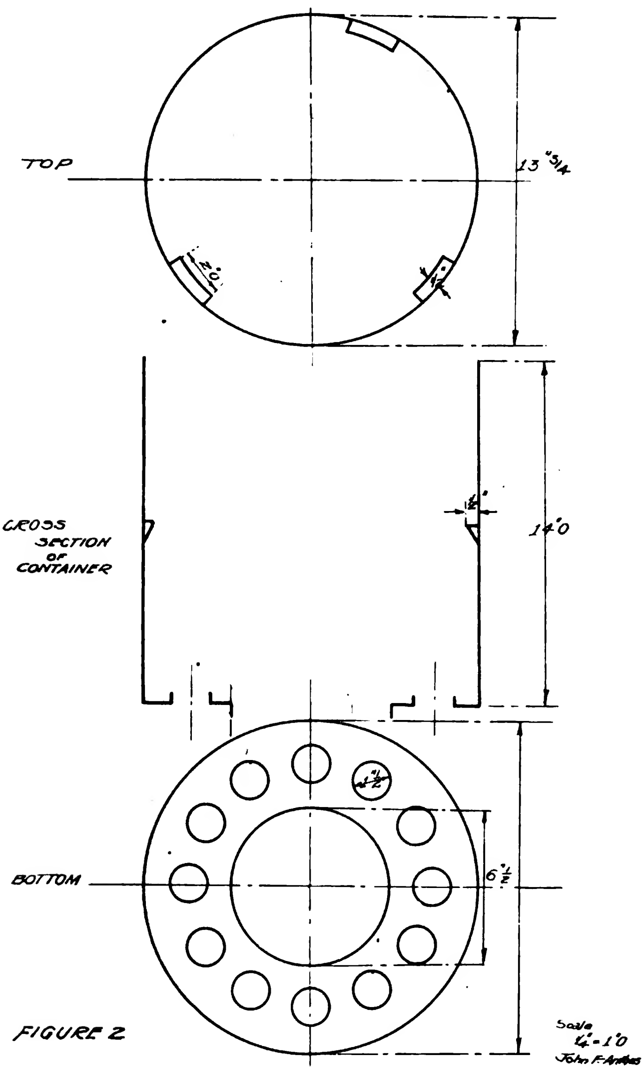


FIGURE 1

Scale 1/4" = 1' 0"
John F. Arthur

15 inches in diameter and 15 inches deep. The glass tubes, which contain the samples of leather, are closed at the top by means of

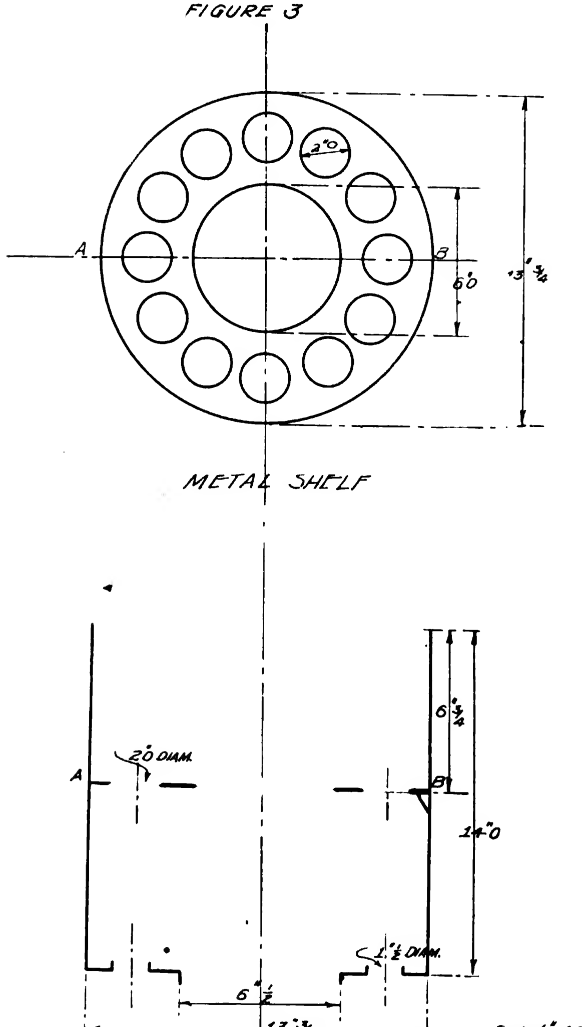
a one-hole rubber stopper, and at the bottom of the glass tubes rubber tubes are attached leading to flasks which receive the



extract. The accompanying cuts illustrate the apparatus in operation, and also give details and dimensions required for its construction.

To operate the apparatus the usual 30-gram sample is placed in the glass extraction tubes between two layers of absorbent

FIGURE 3



CONTAINER WITH METAL SHELF

cotton as shown in Fig. 4. The tubes are then placed in position, the pinch cocks closed, and filled about two-thirds full with

distilled water and allowed to stand over night in the usual manner.

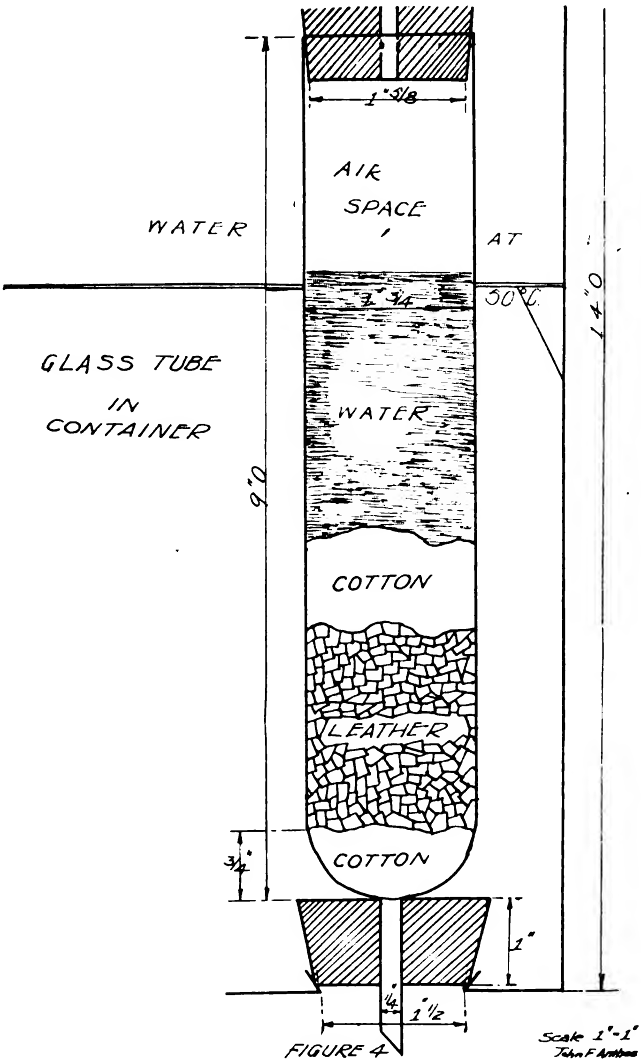


FIGURE 4

The apparatus is then filled with distilled water as shown in Fig. 1 and brought to 50° C. by means of Bunsen burner. When

this temperature has been obtained and remains constant for 15 minutes percolation is started and the two liter samples collected in the usual 3-hour period. For each drop leaving the tube another is forced to enter through the hole in the rubber stopper by the slight vacuum created. The air seal effectively prevents any communication between the water in the tube and that in the bath. If at any time it is desirable to empty any one of the tubes without interfering with or disturbing any other tube, this can be done by inserting a tight-fitting glass tube sufficiently long to reach above the surface of the water, in the small opening in the rubber stopper which is placed in the large tube.

An experiment was made in which fuschine was added to the leather samples and allowed to stand over night, the tubes being completely covered with water, the extraction then proceeded with in the usual way. No trace of color could be observed in the water in the bath. There is no difficulty in keeping the temperature constant to within 1/10 of a degree. The apparatus is kept filled by simply adding distilled water previously heated to 50° to the tank.

In constructing another apparatus a bottom outlet should be provided and a suitable arrangement could easily be made for maintaining a constant supply of distilled water in the tank. The dimensions of the glass tubes are given in Fig. 4. These tubes are made of soft glass and no trouble has been experienced by having the tubes break in the bath. These are made at a reasonable price by Emil Greiner & Company, 55 Fulton Street, New York.

For comparison the results obtained with this apparatus and those obtained by the use of the apparatus described by W. K. Alsop in this JOURNAL, Vol. 13, 1918, page 142, and those obtained by the use of the Oberfell apparatus described in this JOURNAL, Vol. 11, 1916, page 219, are given by the following figures.

A. The results given were obtained by analysis of the same sample of leather prepared for another purpose by W. K. Alsop. Those given in column No. 1 were obtained by J. B. Churchill, using the apparatus described.

The results given in column No. 2 were obtained at the labora-

tory of the Elk Tanning Company by W. K. Alsop and those in column No. 3 by L. M. Whitmore at the Bureau of Standards.

The moisture as reported from all three sources was practically the same; namely, 10.1 per cent.

The results given in column No. 1 were obtained on various extractions carried out over a period of two weeks, not more than two being run at the same time. Of the results given in column No. 2, numbers 1 to 8 inclusive were obtained from extractions made at the same time, numbers 9 to 12 from extractions made two weeks later, while the remaining were determined three months after the first. The results given in column No. 3 were obtained from extractions made on three separate dates.

TABLE A.

	I Churchill	II Alsop	III Whitmore
1	35.41	34.17	34.10
2	35.51	34.46	33.93
3	35.43	34.03	33.56
4	35.44	33.97	34.09
5	35.42	35.12	34.08
6	34.48	34.93	33.96
7	35.71	35.30	33.20
8	35.84	34.83	——
9	35.09	34.63	——
10	34.41	34.63	——
11	35.51	33.79	——
12	35.78	33.47	——
13	35.36	34.27	——
14	35.50	34.30	——
15	35.53	34.32	——
16	35.33	34.23	——
17	35.40	34.25	——
	Average 35.48	Average 34.39	Average 33.84

B. The following results show the values obtained for the per cent. of water soluble material from ten different leathers extracted with this apparatus and with the Oberfell type. The figures given in the first four columns were obtained by J. B. Churchill with the apparatus described while those in the last column were obtained with the Oberfell apparatus by L. M. Whitmore at the Bureau of Standards.

TABLE B.

	I	II	III Aver.	IV Calculated for 12% moisture	V
1	23.90	23.95	23.93	23.81	22.51
2	23.28	23.12	23.20	23.11	20.98
3	23.29	23.67	23.48	23.45	20.71
4	24.89	24.96	24.93	24.87	23.38
5	24.43	24.42	24.43	24.37	23.06
6	24.38	23.44	23.41	23.21	21.06
7	23.47	23.68	23.58	23.23	21.13
8	22.26	23.08	22.67	22.59	20.84
9	26.00	25.83	25.92	25.58	24.67
10	22.74	22.96	22.85	22.87	21.04

It will be noted that the figures obtained by this modification of the extractor average somewhat higher than those obtained by the use of the other types. We feel that this is due mostly to the fact that the tubes containing the leather to be extracted are completely surrounded with water at 50° and are not open at the top.

The results obtained for glucose corresponding to the figures given for total solids are practically the same for the three different types of extractors used.

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THE EXTRACTION OF GREASE AND OIL FROM LEATHER—COMMITTEE REPORT.

By John Arthur Wilson, Chairman.

For many years petroleum ether has been used quite generally, both here and abroad, for extracting grease and oil from leather; in fact, it is at present the solvent required in our own official method for the determination of fat in vegetable tanned leather. It is not surprising that this solvent has come into such wide use, since it is abundant and cheap, is readily obtained free from impurities, and is chemically very stable. But the advisability of using petrol for determining the grease and oil content of leather has been questioned by Wilson and Kern[1] on the ground that it

[1] This JOURNAL, 13, 138 (1918).

does not dissolve oxidized and hydroxylated fatty acids, which are common constituents of finished leathers. They found that either carbon tetrachloride or ethyl ether would dissolve much more of what was apparently fat, from several samples of leather, than would petrol.

Levi and Orthmann[2] made comparative tests with petrol and a mixture of equal volumes of ethyl ether and carbon tetrachloride, which mixture had been recommended for examination by Wilson and Kern. In concluding their paper, Levi and Orthmann said: "We cannot entertain the suggestion to substitute petrolic ether with this new solvent, concordant results may possibly be obtained on chrome leathers, but we doubt if all the extractive could be termed as fat or grease. This surely holds true of vegetable-tanned leather as shown in our results." Wilson and Kern were about to reply when the announcement was made of the appointment of the present committee; it was then deemed wise to wait and let the question be settled by the findings of the committee.

Laboratories and Personnel of the Committee.

A. F. Gallun & Sons Co., Milwaukee, Wis. John Arthur Wilson, Chairman. Erwin J. Kern assisted by Edwin A. Gallun, Alois Krombholz, and Rudolph Olson.

Pfister & Vogel Leather Co., Milwaukee, Wis. August C. Orthmann assisted by Edna F. Hibbert.

American Leather Research Laboratory, New York City. J. B. Churchill assisted by Alexander B. Young.

Leather and Paper Laboratory, Bureau of Chemistry, Washington, D. C. F. P. Veitch assisted by Ralph W. Frey and I. D. Clarke.

The Reed Laboratories, New York City. Robert Wright.

Kistler, Lesh & Co., Morganton, N. C. J. S. Rogers assisted by H. L. Riddle.

Kistler Leather Co., Lock Haven, Pa. J. M. Seltzer assisted by Harry Gordon.

Object.

The fundamental purpose of the committee is to devise and present to the Association the best possible method for determining the amount of fatty matters in leather, but the more immediate object is simply to ascertain which is the best solvent to be used in making the extraction.

[2] This Journal, 13, 313 (1918).

SAMPLES.

The committee had at its disposal 15 samples of leather ranging in weight from shoe upper leather to sole leather and representing chrome, vegetable, and combination tannages. Samples numbered from 1 to 12 were from 6 hides or kips which were cut into sides immediately before treating with fats and only one side of each hide was treated. The analysis of each side was made in the same way, regardless of whether or not it had been fat liquored or stuffed. The shanks, belly, and edges of each side were carefully trimmed off, so that the final contour of any one side was the mirror image of that of its mate and all of the trimmed side was cut up for analysis. The lighter leathers were cut with scissors into pieces about 2 millimeters square, while the heavier leathers were cut by planing. Samples numbered 14 and 15 were furnished by the Leather and Paper Laboratory already cut to a fine powder. Three pairs of sides and one sample of sole leather were furnished by Pfister & Vogel Leather Company and three pairs of sides by A. F. Gallun & Sons Company.

CHAIRMAN'S INSTRUCTIONS REGARDING THE ANALYSES.

Every determination is to be made in duplicate and the actual figures in each case (not the averages) are to be reported. Where possible, it is advisable for the member to turn the duplicate over to an assistant or associate, the name of the analyst to be given with each set of figures. The determinations required are water, fat, matter soluble in water, insoluble ash, and hide substance.

Water.—Dry from 2 to 4 grams of leather to constant weight in an oven at 100° C.

Hide Substance.—Determine the nitrogen by the A. L. C. A. method. Multiply the percentage of nitrogen found by 5.614.

Fat.—Five portions of leather of 7 to 8 grams each are to be extracted by the Soxhlet method for 8 hours, using a different solvent for each portion. The solvents to be used are petroleum ether, ethyl ether, carbon disulphide, carbon tetrachloride, and chloroform. It is recommended that, after extraction, the extract be carefully transferred to a crystallizing dish, such as is used in tannin analysis, and placed in a current of warm air, which can be provided by any ordinary fan. When practically all of

the solvent has evaporated, place the dish in an oven at 90° to 100° C. for 30 minutes, cool in a desiccator for 15 minutes and weigh. Heat in the oven for another 30 minutes, cool, and weigh again. Repeat until the extract does not lose more than a milligram or two in 30 minutes heating. Prolonged heating may cause oxidation to an appreciable extent in some cases and is, therefore, to be avoided. Where convenient, it is suggested that the duplicate fat determinations be run for 12 hours instead of 8.

All solvents used should be reasonably pure and should be redistilled before using. Commercial ethyl ether usually contains both water and alcohol, which should be removed by treating with sodium metal for several hours and then distilling off the ether. Only that portion of the petroleum ether distilling below 80° C. should be used.

Matter Soluble in Water.—The five portions of leather used for fat extraction are to be placed in a current of warm air until free from solvent and each portion is to be extracted separately for water solubles, the final extract being made up to a liter, of which 150 cc. are to be evaporated to constant weight.

For any member not having a regular apparatus for this determination, the following procedure is recommended: Carefully transfer all of the leather from the fat-extraction thimble to a clock glass. When all of the solvent has evaporated, transfer to a clean linen bag which can be closed like an ordinary tobacco bag. Place in a beaker and cover with about 150 cc. of water at 50° C. and let stand in a warm place over night (preferably in an oven kept at 50° C.). Make an extractor as follows: Take a tin can about 6 inches high and cut a hole in the bottom to fit a large rubber stopper and then insert a Soxhlet extraction tube. Cut a hole in the lid of the can and place over the tube. Fill the can surrounding the tube with water at 60° C. immediately before using. Place a liter flask below the Soxhlet tube. Transfer the linen bag containing the leather to the Soxhlet and pour over it the solution in which it was soaking over night, allowing the overflow to be collected in the flask below. Set up a bottle of water at 60° C. with siphon tube and stopcock in such a way as to allow the water to drip into the Soxhlet at the rate of about 300 cc. per hour, or rather so that after extracting for 3 hours

the volume of extract shall be about 950 cc. Make up to a liter and then evaporate 150 cc. to constant weight. Time can be saved by inserting 6, or even 12, Soxhlets in one large can or tank; the larger bulk of water holds the heat better and, therefore, needs less attention. Any devices arranged to keep the temperature of all water used constant at 50° C. is, of course, much to be preferred.

Insoluble Ash.—Place the leather, after extracting the water soluble matter, in a current of warm air until nearly dry. Then transfer to a platinum dish. Ash with a very low flame and weigh.

Any deviations from the above methods should be noted in the report.

Reasons for Procedure Adopted.

The most direct method of testing the effectiveness of a given solvent would naturally be to use it to extract the fat from a portion of the leather sample, weighing the total extract after evaporation of the solvent, and then determining the amount of foreign matters extracted along with the fat. Such procedure, however, would require a greater knowledge of greases and oils than we should be free to attribute to the average leather chemist, especially in the matter of differentiating between the various kinds of oxidized fats and fatty acids and other organic matter which may have been extracted from the leather, where extreme accuracy would be required. Indirect methods are perhaps less satisfactory as a rule, but in this case seemed to offer the only means of getting anything suitable for committee work.

The plan employed consisted of taking a whole hide immediately before fat liquoring and cutting it into sides, only one of which was fat liquored or stuffed. When dried to the same extent, the two sides are assumed to be identical, excepting for the alteration in composition caused by one side having more fat than the other. It is further assumed that, if the solvent extracts x parts of matter (whether fat or not) per 100 parts of hide substance from the unstuffed side, it will extract these same x parts of matter per 100 parts of hide substance from the stuffed side along with nothing else but y parts of the added grease. Since

we can readily determine x from the unstuffed leather and $x + y$ from the stuffed leather, we can calculate the value of y by difference. If our assumptions are correct, then that solvent giving the greatest value for y is most efficient in removing the *added* fats. This gives us a means of determining the relative efficiencies of all the solvents.

Of the available solvents only the five most promising were selected, the examination of this number representing about all the work one could reasonably expect from a committee of this kind in the six months allowed for forming the committee, preparing and distributing samples, directing the course of the work, carrying on a discussion by mail, and writing up the report for publication.

It was considered advisable to determine the soluble matter and insoluble ash in the leather in order to detect any possible action of the solvent upon these constituents.

The results returned by the members appear in Tables I to XV inclusive and are placed in the order in which they were received.

Wherever the term "fat" is used in this paper, it is meant to include all greases, oils, waxes, and fatty acids as well.

General Comments.

The correspondence between the chairman and committee members was so voluminous that only the more salient points can be given here.

Veitch, Frey, and Clarke: All fat determinations were made with the Johnson type of extraction apparatus which is based upon percolation instead of syphoning, and possesses several desirable features as compared with the Soxhlet. Since probably most of the laboratories use the Soxhlet apparatus it was deemed advisable to accept this opportunity to incidentally compare results between the two types. With the Johnson apparatus about 75 cc. of solvent is used and is refluxed from an ordinary weighed 100 cc. Erlenmeyer flask. After extraction, the solvent is evaporated from the flask and the fat weighed directly without any transferring. This apparatus is more compact, especially in battery formation, than the Soxhlet and all

TABLE I.

Sample No. 1.—The left side of a vegetable-tanned kip taken immediately before fat liquoring. For analysis of the right side of this same kip, see Table II. All figures represent parts of constituent per 100 parts of water-free leather.

Analyst	Time of fat extraction in hours	Hide substance	Petrol			Carbon disulphide			Carbon tetrachloride			Ethyl ether			Chloroform		
			Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash
E. J. Kern........	8	56.22	0.35	9.55	0.12	0.40	10.20	0.12	0.50	9.41	0.13	0.85	10.19	0.12	0.73	9.98	0.12
R. M. Olson	12	55.85	0.33	9.84	0.11	0.41	10.79	0.10	0.56	11.25	0.10	0.96	9.84	0.10	0.76	11.01	0.10
A. C. Orthmann...	8	55.86	0.29	9.03	0.12	0.46	8.67	0.12	0.45	9.06	0.13	0.56	8.83	0.14	0.52	9.03	0.13
E. F. Hibbert	12	55.59	0.28	8.71	0.13	0.39	8.88	0.12	0.45	9.19	0.12	0.57	9.16	0.12	0.54	9.39	0.12
J. B. Churchill....	8	56.40	0.44	11.42	0.15	0.52	11.01	0.18	0.49	11.15	0.21	0.79	11.42	0.14	0.59	11.31	0.25
A. B. Young	8	56.44	0.44	11.35	0.15	0.45	10.77	0.18	0.46	11.04	0.23	0.79	11.30	0.14	0.58	11.01	0.25
R. W. Frey......	10	56.59	0.36	—	—	0.46	—	—	0.56	—	—	1.03	—	—	0.82	—	—
I. D. Clarke	24	56.59	0.34	—	—	0.42	—	—	0.49	—	—	0.93	—	—	0.89	—	—
J. S. Rogers	8	55.98	0.38	—	—	—	—	—	—	—	—	1.01	—	—	—	—	—
H. L. Riddle	8	55.91	0.38	—	—	—	—	—	—	—	—	0.91	—	—	—	—	—
Highest		56.59	0.44	11.42	0.15	0.52	11.01	0.18	0.56	11.25	0.23	1.03	11.42	0.14	0.89	11.31	0.25
Lowest		55.59	0.28	8.71	0.11	0.39	8.67	0.10	0.45	9.06	0.10	0.56	8.83	0.10	0.52	9.03	0.10
Average		56.14	0.36	9.98	0.13	0.44	10.05	0.14	0.50	10.18	0.15	0.84	10.12	0.13	0.68	10.29	0.16

TABLE II.

Sample No. 2.—The right side of a vegetable-tanned kip taken immediately after fat liquoring with moellon degras. For analysis of the left side of this same kip, see Table I. All figures represent parts of constituent per 100 parts of water-free leather.

Analyst	Time of fat extraction in hours	Hide substance	Petrol			Carbon disulphide			Carbon tetrachloride			Ethyl ether			Chloroform		
			Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash
E. J. Kern	8	49.02	11.41	9.72	0.15	12.08	10.74	0.15	12.40	10.29	0.15	13.60	9.97	0.15	13.44	9.77	0.15
A. J. Krombholz	12	48.51	11.50	10.19	0.16	12.03	10.30	0.16	12.89	9.71	0.17	13.50	9.61	0.16	13.70	9.72	0.17
A. C. Orthmann	8	50 24	11.10	8.64	0.18	12.49	9.47	0.16	12.56	8.31	0 16	13.89	8.58	0.17	13.48	8.24	0.17
E. F. Hibbert	12	48.76	11.28	8.29	0.16	12.30	8.89	0.17	12.77	8.37	0.16	14.14	8.40	0.13	13.58	8.32	0.16
J. B. Churchill	8	49.34	11.17	10.21	0 19	11.46	10.17	0.32	12.15	10.21	0.31	13.17	10.13	0.25	13.18	10.19	0.33
A. B. Young	8	49.24	11.19	10.42	0.20	11.64	9.89	0.32	12.15	10.43	0.33	13.15	10.10	0.25	13.19	10.18	0.33
R. W. Frey	10	47.16	10.63	—	—	11.96	—	—	11.90	—	—	13.05	—	—	13.08	—	—
I. D. Clarke	24	47.16	10.62	—	—	11.50	—	—	11.99	—	—	12.80	—	—	12.65	—	—
J. S. Rogers	8	48.51	11.50	—	—	—	—	—	—	—	—	13.12	—	—	—	—	—
H. L. Riddle	8	48.44	11.10	—	—	—	—	—	—	—	—	12.93	—	—	—	—	—
Highest		50.24	11.50	10.42	0.20	12.49	10.74	0.32	12.89	10.43	0.33	14.14	10.13	0.25	13.70	10.19	0.33
Lowest		47.16	10.62	8.29	0.15	11.46	8.89	0 15	11.90	8.31	0.15	12.80	8.40	0.13	12.65	8.24	0.15
Average		48.64	11.15	9.59	0.17	11.93	9.91	0.21	12.35	9.55	0.21	13.34	9.47	0.19	13.29	9.40	0.22

TABLE III.

Sample No. 3.—The left side of a black chrome calf taken after blacking, but immediately before fat liquoring. For analysis of the right side of this same skin, see Table IV. All figures represent parts of constituent per 100 parts of water-free leather.

Analyst	Time of fat extraction in hours	Hide substance	Petrol			Carbon disulphide			Carbon tetrachloride			Ethyl ether			Chloroform		
			Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash
E. J. Kern........	8	78.68	1.05	1.04	8.31	1.32	1.09	8.35	1.40	1.21	8.30	1.41	1.37	8.22	1.68	1.60	8.33
R. M. Olson......	12	77.80	1.11	1.10	8.33	1.39	0.89	8.31	1.55	1.24	8.21	1.50	1.39	8.16	1.75	1.51	8.16
A. C. Orthmann...	8	79.24	1.14	1.72	8.12	1.35	1.82	8.08	1.61	2.02	7.89	1.40	1.94	7.96	1.49	1.91	7.94
E. F. Hibbert.....	12	78.09	1.22	1.33	8.03	1.20	1.48	8.00	1.65	1.67	7.91	1.37	1.67	8.07	1.69	1.55	8.02
J. B. Churchill....	8	78.89	1.21	1.82	8.14	1.40	1.99	8.62	1.62	2.27	8.43	1.44	2.51	7.98	1.55	1.95	8.34
A. B. Young......	8	79.35	1.25	1.85	8.14	1.37	1.96	8.66	1.55	2.10	8.43	1.42	2.22	8.54	1.53	2.03	—
R. W. Frey........	8	78.43	0.98	—	—	1.29	—	—	1.54	—	—	1.41	—	—	1.60	—	—
I. D. Clarke......	24	78.43	1.07	—	—	1.36	—	—	1.62	—	—	1.53	—	—	1.72	—	—
Highest.......		79.35	1.25	1.85	8.33	1.40	1.99	8.66	1.65	2.27	8.43	1.53	2.51	8.54	1.75	2.03	8.34
Lowest.......		77.80	0.98	1.04	8.03	1.20	0.89	8.00	1.40	1.21	7.89	1.37	1.37	7.96	1.49	1.51	7.94
Average......		78.61	1.13	1.48	8.18	1.34	1.54	8.34	1.57	1.75	8.20	1.44	1.85	8.16	1.63	1.76	8.16

TABLE IV.

Sample No. 4.—The right side of a black chrome calf taken immediately after fat liquoring with neats-foot oil and soap. For analysis of the right side of this same skin, see Table III. All figures represent parts of constituent per 100 parts of water-free leather.

Analyst	Time of fat extraction in hours	Hide substance	Petrol			Carbon disulphide			Carbon tetrachloride			Ethyl ether			Chloroform		
			Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash
E. J. Kern	8	73.84	6.98	0.70	7.97	7.22	0.71	8.08	7.90	0.58	7.95	7.41	0.63	7.99	8.27	0.83	7.88
R. M. Olson	12	73.48	7.16	0.39	8.01	7.47	0.70	8.04	8.00	0.42	8.09	7.58	0.50	7.99	8.25	0.60	8.01
A. C. Orthmann	8	73.77	6.96	1.00	7.71	7.39	1.20	7.72	8.02	1.69	7.53	7.75	1.39	7.65	8.24	1.47	7.58
E. F. Hibbert	12	73.99	7.11	0.88	7.88	7.35	1.25	7.73	8.12	1.76	7.49	7.73	1.24	7.72	8.28	1.64	7.60
J. B. Churchill	8	74.41	7.42	1.07	8.09	7.67	1.11	8.08	7.69	1.10	7.89	7.35	1.15	8.18	7.59	1.21	7.91
A. B. Young	8	74.41	7.44	1.13	8.00	7.63	1.09	8.08	7.67	1.13	7.90	7.31	1.15	8.14	7.77	0.92	7.90
R. W. Frey	8	73.71	7.17	—	—	7.78	—	—	8.11	—	—	7.98	—	—	8.41	—	—
I. D. Clarke	24	73.71	7.25	—	—	7.75	—	—	8.08	—	—	8.00	—	—	8.43	—	—
Highest		74.41	7.44	1.13	8.09	7.78	1.25	8.08	8.12	1.76	8.09	8.00	1.39	8.18	8.43	1.64	8.01
Lowest		73.48	6.96	0.39	7.71	7.22	0.70	7.72	7.67	0.42	7.49	7.31	0.50	7.65	7.59	0.60	7.58
Average		73.92	7.19	0.86	7.94	7.53	1.01	7.96	7.95	1.11	7.81	7.64	1.01	7.95	8.16	1.11	7.81

TABLE V.

Sample No. 5.—The left side of a hide tanned in chrome and retanned in vegetable liquors, taken immediately before stuffing. For analysis of the right side of this same hide, see Table VI. All figures represent parts of constituent per 100 parts of water-free leather.

Analyst	Time of fat extraction in hours	Hide substance	Petrol			Carbon disulphide			Carbon tetrachloride			Ethyl ether			Chloroform		
			Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash
E. J. Kern	8	63.20	0.36	6.30	4.42	0.49	6.14	4.41	0.57	5.97	4.42	0.60	5.91	4.41	0.75	6.11	4.42
A. J. Kromblholz	12	63.76	0.38	5.30	4.32	0.50	5.11	4.43	0.60	5.86	4.45	0.64	5.43	4.39	0.74	5.16	4.45
A. C. Orthmann	8	63.67	0.31	6.01	4.27	0.48	5.61	4.27	0.59	5.43	4.23	0.61	5.21	4.31	0.58	4.82	4.41
E. F. Hibbert	12	62.45	0.37	5.74	4.30	0.52	5.61	4.38	0.65	5.59	4.25	0.67	5.13	4.27	0.87	5.13	4.26
J. B. Churchill	8	63.05	0.43	6.38	4.51	0.42	6.72	4.52	0.51	6.66	4.42	0.52	6.55	4.52	0.64	6.58	4.40
A. B. Young	8	63.05	0.47	6.35	4.47	0.51	6.37	4.54	0.50	6.79	4.43	0.54	6.35	4.44	0.61	6.15	4.40
R. W. Frey	8	63.61	0.29	—	—	0.40	—	—	0.48	—	—	0.52	—	—	0.75	—	—
I. D. Clarke	24	63.61	0.29	—	—	0.43	—	—	0.55	—	—	0.56	—	—	0.70	—	—
R. Wright	8	64.13	0.37	5.97	4.13	0.52	5.30	4.29	0.61	5.66	4.55	0.53	5.71	4.56	0.64	5.87	4.39
R. Wright	8	64.25	0.36	—	—	0.43	—	—	0.63	—	—	0.55	—	—	0.67	—	—
J. S. Rogers	8	63.27	0.35	—	—	—	—	—	—	—	—	0.58	—	—	—	—	—
H. L. Riddle	8	63.40	0.35	—	—	—	—	—	—	—	—	0.59	—	—	—	—	—
J. M. Seltzer and H. Gordon	8	—	0.43	—	—	0.55	—	—	0.83	—	—	0.79	—	—	0.81	—	—
Highest		64.25	0.47	6.38	4.51	0.55	6.72	4.54	0.83	6.79	4.55	0.79	6.55	4.56	0.87	6.58	4.45
Lowest		62.45	0.29	5.30	4.13	0.40	5.30	4.27	0.48	5.43	4.23	0.52	5.13	4.27	0.58	4.82	4.26
Average		63.45	0.37	6.01	4.35	0.48	5.88	4.41	0.59	5.99	4.39	0.59	5.76	4.41	0.71	5.69	4.39

TABLE VI.

Sample No. 6.—The right side of a hide tanned in chrome and retanned in vegetable liquors, taken immediately after stuffing with stearine and paraffine containing a small amount of wool grease. For analysis of the left side of this same hide, see Table V. All figures represent parts of constituent per 100 parts of water-free leather.

Analyst	Time of fat extraction in hours	Hide substance	Petrol			Carbon disulphide			Carbon tetrachloride			Ethyl ether			Chloroform		
			Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash
E. J. Kern...... .	8	43.58	32.75	3.89	2.94	33.08	4.09	2.93	33.25	3.85	2.95	34.11	3.56	2.94	34.58	3.41	2.99
R. M. Olson.... .	12	42.99	32.77	3.84	3.02	33.74	3.94	2.99	33.03	4.04	3.02	34.12	2.77	3.02	34.67	3.41	3.07
A. C. Orthmann..	8	42.59	32.30	4.23	2.85	32.23	4.19	2.82	32.74	3.78	2.81	33.43	3.53	2.81	33.36	3.32	2.84
E. F. Hibbert.....	12	42.40	32.17	4.10	2.86	32.58	3.87	2.84	33.22	3.52	2.80	33.53	—	2.82	33.73	—	2.82
J. B. Churchill....	8	42.97	32.17	4.17	3.13	32.73	3.65	3.03	33.28	3.95	2.95	33.12	4.15	3.08	32.93	4.01	3.04
A. B. Young......	8	42.99	32.17	4.12	3.10	33.08	4.09	3.16	33.17	4.06	2.96	33.10	3.95	3.21	33.12	3.48	3.04
R. W. Frey......	8	42.72	31.37	—	—	32.05	—	—	32.36	—	—	32.97	—	—	33.31	—	—
I. D. Clarke.......	24	42.72	31.81	—	—	32.56	—	—	32.65	—	—	33.24	—	—	33.80	—	—
R. Wright........	8	42.92	31.99	4.12	3.03	32.85	3.96	3.16	32.82	3.97	2.93	33.06	4.13	3.10	33.08	3.88	3.05
R. Wright........	8	42.92	32.17	—	—	33.12	—	—	32.98	—	—	33.03	—	—	33.16	—	—
J. M. Seltzer and H. Gordon......	8	—	32.43	—	—	32.83	—	—	32.66	—	—	33.35	—	—	33.25	—	—
Highest		43.58	32.77	4.23	3.13	33.74	4.19	3.16	33.28	4.06	3.02	34.12	4.15	3.21	34.67	4.01	3.07
Lowest		42.40	31.37	3.84	2.85	32.05	3.65	2.82	32.36	3.52	2.80	32.97	2.77	2.81	32.93	3.32	2.82
Average		42.88	32.19	4.07	2.99	32.80	3.97	2.99	32.92	3.88	2.92	33.37	3.16	3.00	33.54	3.59	2.98

TABLE VII.

Sample No. 7.—The left side of a vegetable-tanned hide taken immediately before fat liquoring and stuffing. For analysis of the right side of this same hide, see Table VIII. All figures represent parts of constituent per 100 parts of water-free leather.

Analyst	Time of fat extraction in hours	Hide substance	Petrol			Carbon disulphide			Carbon tetrachloride			Ethyl ether			Chloroform		
			Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash
E. J. Kern	8	56.92	0.27	10.13	0.08	0.34	9.70	0.08	0.34	9.81	0.07	0.50	9.16	0.08	0.55	10.15	0.07
A. J. Krombholz	12	56.26	0.28	9.72	0.10	0.39	10.30	0.09	0.34	11.35	0.08	0.56	11.05	0.07	0.61	9.83	0.08
A. C. Orthmann	8	56.81	0.22	11.66	0.10	0.34	12.01	0.12	0.48	11.09	0.11	0.61	11.23	0.10	0.73	11.30	0.09
E. F. Hibbert	12	55.83	0.27	11.51	0.10	0.37	11.50	0.10	0.50	10.99	0.10	0.72	11.66	0.11	0.78	11.46	0.09
J. B. Churchill	8	57.81	0.28	13.90	0.16	0.34	13.41	0.14	0.37	13.62	0.23	0.44	14.00	0.17	0.58	13.18	0.21
A. B. Young	8	57.65	0.33	13.92	0.14	0.34	13.29	0.19	0.46	13.42	0.16	0.48	14.27	0.24	0.54	13.39	0.16
R. W. Frey	8	56.48	0.23	—	—	0.30	—	—	0.37	—	—	0.54	—	—	0.79	—	—
I. D. Clark	24	56.48	0.26	—	—	0.31	—	—	0.35	—	—	0.44	—	—	0.78	—	—
R. Wright	8	56.34	0.29	10.79	0.17	0.35	11.08	0.16	0.41	10.84	0.16	0.46	11.21	0.16	0.66	10.69	0.16
R. Wright	8	56.10	0.34	—	—	0.37	—	—	0.45	—	—	0.52	—	—	0.62	—	—
J. M. Seltzer and H. Gordon	8	—	0.37	—	—	0.43	—	—	0.52	—	—	0.90	—	—	0.66	—	—
Highest		57.81	0.37	13.92	0.17	0.43	13.41	0.19	0.52	13.62	0.23	0.90	14.27	0.24	0.79	13.39	0.21
Lowest		55.83	0.22	9.72	0.08	0.30	9.70	0.08	0.34	9.81	0.07	0.44	9.16	0.07	0.54	9.83	0.07
Average		56.67	0.29	11.66	0.12	0.35	11.61	0.13	0.42	11.59	0.13	0.56	11.80	0.17	0.66	11.43	0.12

TABLE VIII.

Sample No. 8.—The right side of a vegetable-tanned hide taken immediately after fat liquoring with sod oil and soap and stuffing with stearine. For analysis of the left side of this same hide, see Table VII. All figures represent parts of constituent per 100 parts of water-free leather.

Analyst	Time of fat extraction in hours	Hide substance	Petrol			Carbon disulphide			Carbon tetrachloride			Ethyl ether			Chloroform		
			Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash
E. J. Kern...... ..	8	50.76	10.52	9.44	0.09	11.15	9.77	0.09	11.25	9.34	0.09	12.33	9.69	0.08	12.75	9.40	0.09
A. J. Krombholz..	12	50.00	10.40	9.91	0.08	11.55	11.26	0.09	11.36	12.02	0.10	12.24	10.75	0.10	12.55	8.68	0.09
A. C. Orthmann...	8	50.80	10.66	9.21	0.09	11.48	9.60	0.10	12.14	8.51	0.10	12.62	9.74	0.07	12.89	9.33	0.09
E. F. Hibbert.....	12	50.10	10.88	9.85	0.08	11.59	9.39	0.09	12.26	8.40	0.07	13.05	9.21	0.08	13.10	9.41	0.09
J. B. Churchill....	8	50.51	10.95	10.94	0.29	12.31	10.69	0.23	12.39	10.95	0.18	12.61	10.87	0.24	12.45	10.86	0.16
A. B. Young......	8	50.45	11.03	11.28	0.24	12.34	10.73	0.21	12.40	10.66	0.23	12.67	10.49	0.27	12.39	10.87	0.23
R. W. Frey.......	8	50.25	10.28	—	—	10.81	—	—	11.45	—	—	12.04	—	—	11.94	—	—
I. D. Clarke......	24	50.25	10.38	—	—	11.11	—	—	11.52	—	—	12.18	—	—	12.37	—	—
R. Wright........	8	49.76	10.53	9.07	0.18	11.26	8.07	0.17	11.47	8.32	0.16	12.11	8.39	0.18	12.26	8.20	0.21
R. Wright........	8	49.89	10.44	—	—	11.34	—	—	11.01	—	—	12.18	—	—	12.23	—	—
J. M. Seltzer and H. Gordon......	8	—	10.70	—	—	11.13	—	—	11.13	—	—	12.38	—	—	12.33	—	—
Highest		50.80	11.03	11.28	0.29	12.34	11.26	0.23	12.40	12.02	0.23	13.05	10.87	0.27	13.10	10.87	0.23
Lowest		49.76	10.28	9.07	0.08	10.81	8.07	0.09	11.01	8.32	0.07	12.04	8.39	0.07	11.94	8.20	0.09
Average		50.28	10.62	9.96	0.17	11.46	9.93	0.14	11.67	9.74	0.13	12.40	9.88	0.15	12.48	9.54	0.14

TABLE IX.

Sample No. 9.—The left side of a chrome-tanned kip taken immediately before fat liquoring. After tanning, this kip was washed free from soluble mineral matter and then fat liquored without coloring. For analysis of the right side of this same kip, see Table X. All figures represent parts of constituent per 100 parts of water-free leather.

Analyst	Time of fat extraction in hours	Hide substance	Petrol			Carbon disulphide			Carbon tetrachloride			Ethyl ether			Chloroform		
			Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash
E. J. Kern	8	86.23	0.53	0.76	6.87	0.73	0.72	6.91	0.84	0.63	6.91	0.82	0.86	6.87	0.98	0.84	6.91
R. M. Olson	12	86.00	0.46	0.72	6.92	0.70	0.99	6.91	0.90	0.83	6.89	0.88	0.72	6.92	1.01	0.96	6.93
A. C. Orthmann	8	87.57	0.59	0.46	6.73	0.79	0.64	6.76	0.91	0.53	6.77	0.80	0.50	6.70	0.99	0.66	6.71
E. F. Hibbert	12	88.01	0.52	0.48	6.97	0.76	0.52	6.96	0.89	0.59	6.83	0.63	0.61	6.78	0.98	0.50	6.80
J. B. Churchill	8	86.00	0.63	1.10	7.08	0.69	0.96	6.97	0.82	1.19	7.08	0.77	1.10	7.07	0.94	1.52	7.01
A. B. Young	8	86.21	0.66	1.05	6.95	0.67	1.10	6.97	0.79	1.36	6.98	0.80	1.33	7.09	0.93	1.47	6.97
R. W. Frey	8	88.08	0.40	—	—	0.56	—	—	0.69	—	—	0.60	—	—	0.87	—	—
I. D. Clarke	24	88.08	0.48	—	—	0.69	—	—	0.63	—	—	0.77	—	—	0.79	—	—
J. S. Rogers	8	87.49	0.56	—	—	—	—	—	—	—	—	0.84	—	—	—	—	—
H. L. Riddle	8	87.68	0.59	—	—	—	—	—	—	—	—	0.83	—	—	—	—	—
J. M. Seltzer and H. Gordon	8	—	0.50	—	—	0.88	—	—	0.97	—	—	0.70	—	—	1.01	—	—
Highest		88.08	0.66	1.10	7.08	0.88	1.10	6.97	0.97	1.36	7.08	0.88	1.33	7.09	1.01	1.52	7.01
Lowest		86.00	0.40	0.46	6.73	0.56	0.52	6.76	0.63	0.53	6.77	0.60	0.50	6.70	0.79	0.50	6.71
Average		87.14	0.54	0.76	6.92	0.72	0.82	6.91	0.83	0.86	6.91	0.77	0.85	6.91	0.94	0.99	6.89

TABLE X.

Sample No. 10.—The right side of a chrome-tanned kip taken immediately after fat liquoring with sulphonated neats-foot oil. For analysis of the left side of this same kip, see Table IX. All figures represent parts of constituent per 100 parts of water-free leather.

Analyst	Time of fat extraction in hours	Hide substance	Petrol			Carbon disulphide			Carbon tetrachloride			Ethyl ether			Chloroform		
			Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash
E. J. Kern	8	80.27	5.42	0.67	6.18	6.49	0.59	6.18	7.11	0.63	6.18	6.00	0.59	6.19	7.75	0.59	6.17
E. A. Gallun	12	80.06	4.68	0.79	6.23	6.29	0.62	6.24	7.62	0.63	6.17	6.30	0.58	6.19	7.84	0.59	6.19
A. C. Orthmann	8	79.70	4.94	0.78	6.15	6.16	0.87	6.25	7.48	0.80	6.06	6.17	0.95	6.24	7.67	0.82	6.08
E. F. Hibbert	12	80.14	5.01	0.75	6.32	6.35	0.85	6.28	7.27	0.84	6.14	6.50	0.91	6.35	7.40	0.85	6.11
J. B. Churchill	8	80.19	5.71	0.82	6.26	6.41	1.04	6.44	7.53	1.21	6.44	6.71	1.11	6.50	7.71	1.30	6.29
A. B. Young	8	80.41	5.62	0.70	6.25	6.25	1.10	6.47	7.53	1.21	6.40	6.75	0.94	6.47	7.65	1.29	6.37
R. W. Frey	8	80.84	3.71	—	—	4.63	—	—	5.60	—	—	4.97	—	—	7.07	—	—
I. D. Clarke	24	80.84	3.99	—	—	5.13	—	—	5.93	—	—	5.46	—	—	7.14	—	—
J. S. Rogers	8	79.00	4.33	—	—	—	—	—	—	—	—	5.64	—	—	—	—	—
H. L. Riddle	8	79.20	4.44	—	—	—	—	—	—	—	—	5.79	—	—	—	—	—
J. M. Seltzer and H. Gordon	8	—	4.45	—	—	5.46	—	—	6.66	—	—	5.77	—	—	6.82	—	—
Highest		80.84	5.71	0.82	6.32	6.49	1.10	6.47	7.62	1.21	6.44	6.75	1.11	6.50	7.84	1.30	6.37
Lowest		79.00	3.71	0.67	6.15	4.63	0.59	6.18	5.60	0.63	6.06	4.97	0.58	6.19	6.82	0.59	6.08
Average		80.07	4.75	0.75	6.23	5.91	0.85	6.31	6.97	0.89	6.23	6.01	0.85	6.32	7.45	0.91	6.20

TABLE XI.

Sample No. 11.—The right side of a chrome and vegetable-tanned kip taken immediately before fat liquoring. For analysis of the left side of this same kip, see Table XII. All figures represent parts of constituent per 100 parts of water-free leather.

Analyst	Time of fat extraction in hours	Hide substance	Petrol			Carbon disulphide			Carbon tetrachloride			Ethyl ether			Chloroform		
			Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash
E. J. Kern........	8	59.15	0.55	4.59	2.25	0.64	5.30	2.25	0.82	4.58	2.27	0.76	4.74	2.21	0.82	4.59	2.26
E. A. Gallun.	12	58.90	0.54	5.68	2.22	0.67	5.57	2.23	0.77	5.51	2.18	0.82	5.52	2.19	0.95	5.49	2.20
A. C. Orthmann...	8	58.40	0.57	5.32	2.15	0.67	5.35	2.21	0.75	4.54	2.18	0.89	5.03	2.18	0.92	4.60	2.17
E. F. Hibbert....	12	57.80	0.54	5.17	2.18	0.69	4.95	2.19	0.82	4.62	2.18	0.99	4.78	2.16	1.02	5.09	2.22
J. B. Churchill....	8	59.34	0.[illegible]8	5.16	2.28	0.59	5.56	2.23	0.73	5.18	2.28	0.83	5.16	2.30	0.71	5.23	2.30
A. B. Young......	8	59.37	0.39	5.25	2.26	0.64	5.68	2.26	0.71	5.17	2.28	0.82	5.17	2.30	0.72	5.15	2.30
R. W. Frey.......	8	59.73	0.55	—	—	0.64	—	—	0.68	—	—	0.71	—	—	0.81	—	—
I. D. Clarke......	24	59.73	0.56	—	—	0.65	—	—	0.71	—	—	0.79	—	—	0.91	—	—
R. Wright........	8	59.56	0.64	4.51	2.22	0.80	4.62	2.22	0.88	4.23	2.24	0.98	4.32	2.26	1.13	4.20	2.28
R. Wright	8	59.42	0.67	—	—	0.76	—	—	0.86	—	—	1.08	—	—	0.96	—	—
J. M. Seltzer and H. Gordon......	8	—	0.65	—	—	0.71	—	—	0.70	—	—	1.02	—	—	0.91	—	—
Highest		59.73	0.67	5.68	2.28	0.80	5.68	2.26	0.88	5.51	2.28	1.08	5.52	2.30	1.13	5.49	2.30
Lowest.		57.80	0.38	4.51	2.15	0.59	4.62	2.19	0.68	4.23	2.18	0.71	4.32	2.16	0.71	4.20	2.17
Average		59.14	0.55	5.10	2.22	0.68	5.29	2.23	0.77	4.83	2.23	0.88	4.96	2.23	0.90	4.91	2.25

TABLE XII.

Sample No. 12.—The left side of a chrome and vegetable-tanned kip taken immediately after fat liquoring with sod oil and soap and stuffing with stearine. For analysis of the right side of this same kip, see Table XI. All figures represent parts of constituent per 100 parts of water-free leather.

Analyst	Time of fat extraction in hours	Hide substance	Petrol			Carbon disulphide			Carbon tetrachloride			Ethyl ether			Chloroform		
			Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash
E. J. Kern	8	42.00	26.89	4.32	1.32	27.20	4.42	1.34	27.25	4.55	1.35	28.08	3.86	1.32	28.56	4.42	1.33
E. A. Gallun	12	42.32	27.09	4.76	1.28	27.58	4.16	1.33	27.74	4.49	1.26	28.42	3.90	1.27	28.50	4.36	1.29
A. C. Orthmann	8	42.01	26.29	3.76	1.25	27.48	3.79	1.27	27.29	3.46	1.26	28.09	3.57	1.27	28.30	3.54	1.27
E. F. Hibbert	12	41.23	26.43	3.87	1.27	26.95	3.68	1.27	27.41	3.38	1.28	28.17	3.86	1.27	28.25	3.60	1.26
J. B. Churchill	8	42.13	26.84	4.45	1.37	27.00	4.50	1.41	27.25	3.80	1.40	27.80	4.53	1.40	27.61	3.99	1.49
A. B. Young	8	41.98	26.61	4.45	1.33	26.95	4.09	1.38	27.22	4.17	1.38	28.05	4.49	1.44	27.92	4.17	1.37
R. W. Frey	8	42.72	26.52	—	—	26.69	—	—	26.85	—	—	27.34	—	—	27.56	—	—
I. D. Clarke	24	42.72	26.08	—	—	26.97	—	—	27.35	—	—	27.48	—	—	28.11	—	—
R. Wright	8	41.56	25.94	3.76	1.37	26.81	3.92	1.38	27.33	3.62	1.38	27.93	3.65	1.42	28.09	3.25	1.42
R. Wright	8	41.68	26.22	—	—	26.89	—	—	27.22	—	—	27.87	—	—	27.79	—	—
J. M. Seltzer and H. Gordon	8	—	26.55	—	—	27.28	—	—	27.43	—	—	28.11	—	—	28.02	—	—
Highest		42.72	27.09	4.76	1.37	27.58	4.50	1.41	27.74	4.55	1.40	28.42	4.53	1.44	28.56	4.42	1.49
Lowest		41.23	25.94	3.76	1.25	26.69	3.68	1.27	26.85	3.38	1.26	27.34	3.57	1.27	27.56	3.25	1.26
Average		42.04	26.50	4.20	1.31	27.07	4.08	1.34	27.29	3.92	1.33	27.94	3.98	1.34	28.06	3.90	1.35

TABLE XIII.

Sample No. 13.—Sole leather.

Analyst	Time of fat extraction in hours	Hide substance	Petrol			Carbon disulphide			Carbon tetrachloride			Ethyl ether			Chloroform		
			Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash
E. J. Kern........	8	38.21	3.48	26.67	0.11	3.58	27.83	0.11	4.02	28.05	0.10	4.19	26.70	0.11	4.36	27.09	0.10
E. A. Gallun......	12	38.50	3.26	27.70	0.10	3.70	25.86	0.11	3.66	26.61	0.17	4.19	26.86	0.13	4.34	27.11	0.10
A. C. Orthmann...	8	38.41	3.29	26 96	0.10	3.62	27.45	0.12	3.70	26.89	0.09	4.60	25.72	0.09	4.27	26.30	0.10
E. F. Hibbert. ...	12	37.79	3.14	27.07	0.13	3.45	27.44	0.10	3.76	27 47	0.11	4.43	25.84	0.11	4.28	26.40	0.09
J. B. Churchill....	8	38.62	3.45	29.85	0.26	3.75	30.20	0.18	4.26	29.20	0.21	4.36	29.22	0.20	4.34	28.73	0.18
A. B. Young......	8	38.62	3.56	29.57	0.22	3.75	30.01	0.22	4.26	29.28	0.18	4.21	29.08	0.18	4.23	28.68	0.18
R. W. Frey.......	8	35.48	3.30	—	—	3.42	—	—	3.30	—	—	3.93	—	—	4.09	—	—
I. D. Clarke.......	24	35.48	3.38	—	—	3.47	—	—	3 83	—	—	4.35	—	—	4.86	—	—
J. S. Rogers.......	8	37.59	3 38	—	—	—	—	—	—	—	—	4.30	—	—	—	—	—
H. L. Riddle......	8	37.47	3.38	—	—	—	—	—	—	—	—	4.16	—	—	—	—	—
J. M. Seltzer and H. Gordon....	8	—	3.26	—	—	3.82	—	—	3.88	—	—	5.35	—	—	4.56	—	—
Highest		38.62	3.56	29.85	0.26	3.82	30.20	0.22	4.26	29.28	0.21	5.35	29.22	0.20	4.86	28.73	0.18
Lowest........		35.48	3.14	26.67	0.10	3.42	25.86	0.10	3.30	26.61	0.09	3.93	25.72	0.09	4.09	26.30	0.09
Average		37.62	3.35	27.97	0.15	3.62	28.13	0.14	3.85	27.92	0.14	4.37	27.24	0.14	4.37	27.39	0.13

TABLE XIV.

Sample No. 14.—Sole leather.

Analyst	Time of fat extraction in hours	Hide substance	Petrol			Carbon disulphide			Carbon tetrachloride			Ethyl ether			Chloroform		
			Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash
E. J. Kern........	8	43.91	2.46	26.15	0.23	2.51	27.39	0.23	2.66	25.37	0.24	2.99	24.09	0.23	3.19	25.17	0.23
E. A. Gallun......	12	44.18	2.49	26.40	0.24	2.62	27.37	0.17	2.64	23.56	0.21	2.87	26.62	0.23	2.99	26.48	0.18
A. C. Orthmann..	8	44.10	2.32	27.20	0.21	2.60	27.20	0.22	2.68	26.71	0.22	3.40	24.77	0.20	3.44	25.81	0.22
E. F. Hibbert.....	12	44.07	2.58	26.64	0.21	2.63	27.09	0.21	2.62	27.15	0.20	3.16	25.15	0.22	3.39	26.05	0.21
J. B. Churchill....	8	41.06	2.55	30.47	0.34	2.73	30.44	0.39	2.68	30.18	0.34	2.94	30.44	0.36	2.82	30.56	0.34
A. B. Young......	8	43.34	2.50	30.19	0.35	2.73	30.27	0.35	2.74	30.13	0.38	2.90	30.60	0.34	2.82	30.49	0.34
R. W. Frey.......	8	43.06	2.52	—	—	2.54	—	—	2.56	—	—	2.98	—	—	3.52	—	—
I. D. Clarke......	24	43.06	2.38	—	—	2.72	—	—	2.76	—	—	3.32	—	—	3.94	—	—
J. S. Rogers.......	8	43.43	2.44	—	—	—	—	—	—	—	—	3.38	—	—	—	—	—
H. L. Riddle......	8	43.50	2.47	—	—	—	—	—	—	—	—	3.46	—	—	—	—	—
J. M. Seltzer and H. Gordon......	8	—	2.51	—	—	2.85	—	—	2.94	—	—	4.06	—	—	3.87	—	—
Highest		44.18	2.58	30.47	0.35	2.85	30.44	0.39	2.94	30.18	0.38	4.06	30.60	0.36	3.94	30.56	0.34
Lowest.... ...		43.06	2.32	26.15	0.21	2.51	27.09	0.17	2.56	23.56	0.20	2.87	24.09	0.20	2.82	25.17	0.18
Average		43.67	2.47	27.84	0.26	2.66	28.22	0.26	2.70	27.18	0.27	3.22	26.95	0.26	3.33	27.43	0.25

TABLE XV.

Sample No. 15.—Chrome retan upper leather.

Analyst	Time of fat extraction in hours	Hide substance	Petrol			Carbon disulphide			Carbon tetrachloride			Ethyl ether			Chloroform		
			Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash	Fat	Water soluble	Insoluble ash
E. J. Kern........	8	53.42	18.62	5.07	2.05	18.69	5.48	2.06	18.91	5.05	2.06	18.86	5.06	2.05	19.23	5.01	2.02
R. M. Olson......	12	52.62	18.53	6.02	2.07	18.74	6.82	2.05	18.91	5.98	2.10	19.04	5.59	2.16	19.40	5.78	2.16
A. C. Orthmann...	8	52.65	17.54	6.28	1.94	17.83	—	—	18.04	6.83	1.91	18.16	6.25	1.90	18.28	6.51	1.90
E. F. Hibbert.....	12	52.19	17.50	6.10	1.93	18.17	6.21	1.92	18.09	6.60	1.92	18.15	6.50	1.90	18.16	6.48	1.95
J. B. Churchill....	8	53.43	17.75	7.18	2.09	18.12	6.87	2.02	17.40	7.01	2.09	18.10	7.04	2.05	18.38	7.38	2.06
A. B. Young......	8	53.18	17.58	7.16	2.05	18.09	6.99	1.99	17.45	7.21	2.01	18.07	7.31	2.06	18.39	7.34	2.06
R. W. Frey.......	8	52.27	17.43	—	—	17.83	—	—	17.81	—	—	17.39	—	—	18.08	—	—
I. D. Clarke	24	52.27	17.72	—	—	17.74	—	—	18.12	—	—	17.18	—	—	18.46	—	—
J. S. Rogers	8	52.89	17.58	—	—	—	—	—	—	—	—	18.18	—	—	—	—	—
H. L. Riddle......	8	52.60	17.73	—	—	—	—	—	—	—	—	18.15	—	—	—	—	—
J. M. Seltzer and H. Gordon......	8	—	17.83	—	—	17.93	—	—	18.37	—	—	18.40	—	—	18.58	—	—
Highest		53.43	18.62	7.18	2.09	18.74	6.99	2.06	18.91	7.21	2.10	19.04	7.31	2.16	19.40	7.38	2.16
Lowest		52.19	17.43	5.07	1.93	17.74	5.48	1.92	17.40	5.05	1.91	17.18	5.06	1.90	18.08	5.01	1.90
Average.......		52.75	17.80	6.30	2.02	18.13	6.47	2.01	18.12	6.45	2.02	18.15	6.29	2.02	18.55	6.42	2.03

parts are inexpensive and easily replaced. Also, a minimum of solvent is used and no transferring to a lighter receptacle for weighing is necessary. It has, however, been stated informally by at least one member of the Association that fat determinations for leather will be considerably higher when the extract is dried and weighed in a flask instead of a more open vessel such as a tannin dish. No data have been published on this point so that it is still an open question. With tannin dishes difficulty has been experienced by this laboratory in preventing loss from creeping during the driving off of the solvent.

On the whole, the results indicate that 8 hours extraction is either not quite sufficient or that the end point for the extraction is not sharp. The average per cent. difference in favor of the 24 hours extraction is for the various solvents as follows: Petrol, 0.06 per cent.; ether 0.11 per cent.; CCl_4, 0.16 per cent.; $CHCl_3$, 0.19 per cent. There may be some significance between these differences and a definite end point during extraction.

It is felt, from preliminary observations only, that chloroform and ethyl ether, these two particularly, extract at times small quantities of something other than greases and related fatty matters. We believe, however, that the error due to this is generally less than that from incomplete extraction by petroleum ether.

Generally speaking, the fat residues from extraction with ether and chloroform respectively were decidedly the darkest, being often a very dark brown. This was particularly noticeable with the two sole leathers No. 13 and No. 14. With these two leathers the material extracted by ether and by chloroform separated into two more or less distinct rings, one slightly colored, the other a very dark brown. The other three solvents gave homogeneous appearing residues. Those from carbon disulphide and carbon tetrachloride being somewhat dark, while those from petroleum ether were the lightest in color. The residues from No. 13 were accidentally discarded before any further examination of them was made, but those from the 24 hours extraction of No. 14 were examined qualitatively for tannin. The residues from chloroform and ether gave appreciable precipitates with gelatine solution and showed the presence of a blue fluorescent body. Those

from carbon disulphide and carbon tetrachloride gave only a slight precipitate with gelatine, but a very strong blue fluorescence when made ammoniacal. The residue from petroleum ether did not respond to either of these tests. Leather No. 14 is a so-called oak leather having about 25 per cent. water soluble matter. Its water extract responds strongly to the fluorescent test.

It is very probable with leathers of the sole leather type, having comparatively large quantities of uncombined tannins, that solvents such as chloroform and ether extract appreciable amounts of material other than fats, oils and greases. Furthermore, with leathers such as this class the fat content is generally very low so that the relative error is rather large.

In this connection the advisability of having two solvents, one for heavily stuffed and lightly tanned leathers, and one for heavily tanned and lightly stuffed leathers is suggested for the consideration of the committee. It may not be very advisable and is merely offered for further discussion.

There is need for further work to show conclusively, if possible, the *absolute* efficiency of various solvents for extracting greases and oils from leather. Independent experiments started by this laboratory several months ago will, it is hoped, give some data on this point.

All nitrogen determinations given after the names of Frey and Clarke were made by the Nitrogen Laboratory of the Bureau of Chemistry and were calculated from the average per cent. nitrogen and the average per cent. moisture. (Note: These figures were returned as per cent. of nitrogen, but the chairman took the privilege of calculating them in terms of hide substance to make them comparable with the results of the other analysts.)

CHURCHILL: The apparatus used for the water soluble determinations was of the type designed by Mr. H. C. Reed, which has given satisfactory results in both this laboratory and his.[3] It consists essentially of a set of 12 glass tubes placed in a large cylindrical, tin-lined, copper container about 15 inches in diameter and 15 inches deep. To the bottom of the glass tubes, rubber tubes were attached, the flow into the flasks being regulated by

[3] This apparatus is described more completely elsewhere in this issue.

an ordinary screw pinch cock. For each drop leaving the tube another was forced to enter through the hole in the stopper by the slight vacuum created. The air seal effectively prevents any communication between the water in the tube and that in the bath. The temperature is easily held to $50° \pm 0.1°$. Distilled water was used for the extractions. I might say that the results obtained with this apparatus are generally a little higher than those obtained with Teas or Oberfell type.

I have had to make a great many extractions where the material could not be extracted in a satisfactory manner with petroleum ether. In a great many cases, I have found that pure benzol has given very excellent results. The other evening in talking with Dr. Parker C. McIlhiney, I was much interested in his statement that he had found benzol a very satisfactory solvent for the extraction of greases and that he used it to a very considerable extent in his work. Frankly I have had no experience with the use of benzol as a solvent for the extraction of leather, but I am wondering if it would not be worth while trying it in connection with this committee work. It seems to me that benzol has certain advantages as a solvent, that it has a constant boiling point, and that it can be obtained in a state of high purity at a fairly low price. Furthermore, it has the advantage of being stable under all conditions and not open to the objection of decomposition such as I have heard several times expressed against chloroform, as a solvent, namely, that on exposure to sunlight it may be more or less decomposed and that the use of such material might cause a variation in the results. Personally I think this objection is not a serious one, if reasonable care is taken to use a grade of chloroform that is apparently free from decomposition products.

I ran some determinations on leather No. 15 and obtained the following results: Moisture 7.93 and grease 16.87 and 16.82. Extraction of sample of harness leather from Hans Rees & Co., moisture 8.76; grease, petrol 12.26 and 12.29; ethyl ether 12.20 and 12.09; chloroform 12.08 and 12.08; benzol 12.09 and 12.06. I think samples like No. 2 and No. 10 might tell the story fairly well.

KERN: Following Churchill's suggestion I used redistilled

benzol for extracting leather No. 10 and found per 100 parts of water-free leather 4.14 parts of grease after 8 hours extraction and 4.65 parts after 12 hours extraction. This shows no advantage over petrol for this particular leather.

In order to test a statement by Orthmann that chloroform would dissolve chrome soaps, I determined the chrome content of the fat extracts from leather No. 10. The fat from the petrol extract gave 0.02 part of chromic oxide per 100 parts of water-free leather, while the chloroform extract gave 0.03 part, both of which are negligible.

Since only one leather of the type of No. 10 was used for the committee work, I took a sample of finished chrome leather which had been fat liquored with a sulphonated oil. The petrol figure for fat content was 3.49 per cent., while the chloroform figure was 6.03 per cent. Of these figures 0.04 per cent. consisted of ash in the case of petrol and 0.13 per cent. in the case of chloroform. It is difficult to see how anything but fat could have been extracted from the leather unless it was some mineral matter such as chrome or other salts. The difference in fat contents cannot be attributed to chrome or salt.

WRIGHT: The water solubles were determined on 16 grams of leather as were also the insoluble ashes. This was done because our leather extractor is made to hold 30 grams of finely ground leather and 8 grams of leather when cut into small pieces, rather than being pulverized, would not be properly extracted with our apparatus. I am not satisfied with my water soluble results since I find that it is difficult to get checks with 30 grams of ground leather as called for in the official methods of the A. L. C. A. and the fact that some of the samples were cut into small pieces, rather than being ground to a fine state of division, makes me hesitate in accepting these results as correct. However, I submit the results as I found them.

The water soluble determinations on the samples of leather submitted were made in an extractor designed by Mr. Reed. It consists of a number of glass tubes placed in a copper container, the tubes protruding through rubber stoppers in the bottom of the container. The glass tubes are 250 cc. in capacity. The leather to be extracted is placed in the tube, the bottom closed

by means of a rubber tube and screw pinch clamp. The leather is then covered with water and a one-hole rubber stopper inserted in the top of the glass tube. The container is then filled with distilled water, the level of the water being about 2 inches above the top of the rubber stopper inserted in the top of the glass tube. The whole apparatus is heated by a Bunsen burner and since there is a large body of water to be heated the temperature is very easily controlled. When ready to extract the leather the screw pinch clamp is opened and for every drop of water that leaves the glass tube another drop is forced in. The glass tube is not entirely filled with water and the air in the top part of the tube acts as a seal preventing the water in the tube mixing with the water in the copper container. We have found this apparatus very satisfactory in use, and wherever possible use 30 grams of finely ground leather for extraction.

In my tests I used Eimer & Amend's petrolic ether, which will practically all distil under 45° C. The official method calls for ether boiling under 80° C., and I would not be surprised if the ether distilling at the higher temperature would extract more matter than the ether ordinarily sold by chemical supply houses. Should petrolic ether still continue to be used under the official methods, it is my opinion that the temperatures should be specified between which the ether distils. For instance, the specification could read "petrolic ether that boils between 70° and 80° C." instead of "petrolic ether boiling under 80° C." I have not had time to investigate this matter, due to the fact that I have been very busy of late, and merely offer it as a suggestion.

ROGERS: The fat residues were dried as follows: After completing an 8-hour extraction the leather was removed from the Soxhlet, the major portion of the solvent distilled into a Soxhlet and recovered. The flasks were then set on a warm surface and the remaining solvent quickly removed by holding a tube, connected with the vacuum, in the neck of the flasks. The flasks were then immediately placed in the drying oven. This procedure I have found more rapid and better than that described, for the following reasons: (1) saving of time; (2) saving of solvent; (3) avoiding possible loss due to transferring; (4) avoiding loss which frequently occurs from the solvent carrying fat over the edges of the dish, when a tannin dish is used.

It does not seem desirable that in the analysis of a leather the fat determination should include soap used in filling the leather.

Regarding the method of preparing the leather samples for analysis, it is possible that samples prepared in different ways may have an influence upon the amount of fat extracted and different fats may react differently in this respect. This matter is simply mentioned for your consideration.

I believe that if the limits of the boiling point of petroleum ether were narrowed and lowered, it would be found to give more concordant and better results.

Argument in Favor of Adopting Chloroform as the Official Solvent.

After the first three laboratories had completed all of the analytic work, in order to save time, the chairman sent to each member an incomplete form of Table XVI along with an argument similar to that given in the section dealing with reasons for procedure adopted. In the column headed "relative efficiency" in Table XVI, the efficiency of the solvent extracting the greatest amount of added fat is taken as 100, and from this the relative efficiencies of the others have been calculated. The argument is based solely upon the relative efficiencies, although the question of absolute efficiency is discussed in a later section. It will be seen from the table that chloroform invariably shows the greatest efficiency.

Leather No. 2 was fat liquored with moellon degras, chosen purposely as a representative of the oxidized fats. By analysis, about 15 per cent. of the total fatty matter of the moellon was found to consist of oxidized fatty acids, and it is, therefore, interesting to note that, with respect to chloroform, petrol is only about 85 per cent. efficient.

Leather No. 10 was especially prepared to demonstrate the action of the solvents upon sulphonated oils. After tanning, the kip was thoroughly washed and an analysis showed that the leather contained no soluble ash. At this stage it was cut in two. Sample No. 9 should, therefore, contain nothing but hide substance, insoluble chrome compounds, traces of insoluble mineral matter, natural animal fats, and water. Sample No. 10 is iden-

tical with No. 9 except for the added sulphonated oil. The proof seems overwhelming that the very marked inferiority of petrol with this leather is due to its inability to remove from the leather certain portions of the sulphonated oil.

In concluding the argument sent to the members, the chairman made the following recommendation:

"Chloroform is clearly the most efficient solvent tried and I therefore recommend that we propose to the Association that chloroform replace petrol as the official solvent until such time as a better solvent is found."

Each member was requested to criticise the argument, to give his own views, and to go on record definitely in the form of a vote as favoring or opposing the recommendation.

Of the seven laboratories engaged in the work, five favored the recommendation, one was non-committal, and one opposed.

Members' Criticisms of the Preceding Argument.

Churchill: May I say that I am thoroughly in favor of adopting chloroform as the official solvent for the accurate extraction of fat in leather. I have no special criticism to make other than to say that I have gone over your recommendations which were enclosed in your letter of January 18th, and have studied very carefully the results given in your table showing the relative efficiencies of the different solvents. I think that your figures show very plainly that chloroform is, under most conditions, the best solvent for fat in leather that we know of at the present time.

Orthmann and Hibbert: Your method of sampling *does not* eliminate all uncertainties regarding the nature of extractive, although it is true that your procedure eliminates any error of uniformity of sample.

In a case of chrome tanned leather, if all the natural fat were combined as a chrome soap there would still be sufficient uncombined chrome salt present to combine with additional fat from fat liquoring, under favorable conditions. In a case of this kind the differences in fat content before and after fat liquoring would not be correct, in the latter the extractive would undoubtedly be higher with other solvents as compared to petrol ether.

TABLE XVI.

Description of leather	Solvent	Parts fat per 100 parts hide substance			
		Before fat liquoring or stuffing	After fat liquoring or stuffing	Increase	Relative efficiency
Samples Nos. 1 and 2.—Vegetable-tanned kip fat liquored with moellon degras.	Petrol	0.64	22.92	22.28	85.3
	Carbon disulphide	0.78	24.53	23.75	91.0
	Carbon tetrachloride	0.89	25.39	24.50	93.8
	Ethyl ether	1.50	27.43	25.93	93.3
	Chloroform	1.21	27.32	26.11	100.0
Samples Nos. 3 and 4.—Black chrome calfskin fat liquored with neats-foot oil and soap.	Petrol	1.44	9.73	8.29	92.4
	Carbon disulphide	1.70	10.19	8.49	94.6
	Carbon tetrachloride	2.00	10.75	8.75	97.5
	Ethyl ether	1.83	10.34	8.51	94.9
	Chloroform	2.07	11.04	8.97	100.0
Samples Nos. 5 and 6.—Chrome and vegetable-tanned hide stuffed with stearine and paraffine, and a small amount of wool grease.	Petrol	0.58	75.07	74.49	96.6
	Carbon disulphide	0.76	76.50	75.74	98.2
	Carbon tetrachloride	0.93	76.77	75.84	98.4
	Ethyl ether	0.93	77.82	76.89	99.7
	Chloroform	1.12	78.22	77.10	100.0

TABLE XVI.—(*Continued*)

Description of leather	Solvent	Parts fat per 100 parts hide substance			
		Before fat liquoring or stuffing	After fat liquoring or stuffing	Increase	Relative efficiency
Samples Nos. 7 and 8.—Vegetable-tanned hide fat liquored with sod oil and soap and stuffed with stearine.	Petrol	0.51	21.12	20.61	87.1
	Carbon disulphide	0.62	22.79	22.17	93.7
	Carbon tetrachloride	0.74	23.21	22.47	94.9
	Ethyl ether	0.99	24.66	23.67	100.0
	Chloroform	1.16	24.82	23.66	100.0
Samples Nos. 9 and 10.—Chrome-tanned kip washed free from soluble mineral matter and then fat liquored with sulphated neats-foot oil.	Petrol	0.62	5.93	5.31	64.6
	Carbon disulphide	0.83	7.38	6.55	79.7
	Carbon tetrachloride	0.95	8.70	7.75	94.3
	Ethyl ether	0.88	7.51	6.63	80.7
	Chloroform	1.08	9.30	8.22	100.0
Samples Nos. 11 and 12.—Chrome and vegetable-tanned kip fat liquored with sod oil and soap and stuffed with stearine.	Petrol	0.93	63.04	62.11	95.2
	Carbon disulphide	1.15	64.39	63.24	96.9
	Carbon tetrachloride	1.30	64.91	63.61	97.5
	Ethyl ether	1.49	66.46	64.97	99.6
	Chloroform	1.52	66.75	65.23	100.0

You base the efficiency of chloroform upon the sole fact that it extracts more matter than any of the other solvents tried by the committee. Complete analyses of the chloroform extractive would be in order before accepting chloroform as an official solvent for extracting fat from leather. In our opinion the work of the committee has not been sufficient to prove that chloroform extracts only fatty matter, having not examined any leather that was finished like upper, etc., or representative of a general line of leathers on the market. Finished leather would contain many other substances than fat and would probably be soluble in chloroform. The leathers that were examined either required no finish or were in the unfinished state.

Chloroform is a solvent for rubber, resins, and sulphur, to some extent, all of which are apt to be present in leather, depending upon the treatment of the tanned or the untanned hide. These substances cannot be classed as grease or oil. Furthermore, chloroform in a pure state is not a stable article, it is partially decomposed by light into HCl, $COCl_2$, Cl, and H_2O. In order to render it stable $\frac{1}{2}$ to 1 per cent. of alcohol must be added and kept in a dark cool place. The slight amount of alcohol would be a detriment, in that alcohol is a solvent for a great many substances that cannot be classed as grease or oil and which may be present in leather.

In conclusion, we urge that the use of petrol ether be continued as the official solvent for the extraction of fat from leather until a solvent has been found that will extract only grease or fatty matter from leather.

VEITCH, FREY, AND CLARKE: Assuming that either the solvents extract only greases, oils, and related fatty matters, or that the treated sample in each case does not undergo changes during and after fat liquoring or stuffing that might effect the "relative extracting efficiency" of the various solvents upon constituents other than fatty matters, the results show that in general chloroform is the most efficient solvent of the five tried. If one solvent must be decided upon, we believe from the data at hand and without having seen the results of the entire committee, that while chloroform does not give as pure fat residues as does petroleum ether, it does give for leathers such as those repre-

sented by the first twelve samples more nearly correct results and should be substituted for petroleum ether until a better solvent is found. More work should, however, be done on leathers of the sole leather type.

SELTZER AND GORDON: We recommend that chloroform be adopted as the official solvent. We are greatly pleased with the action of chloroform from the analytical standpoint as we find that in running the extractions the chloroform does not vaporize and escape from our extraction apparatus as readily as does the petroleum ether, and since chloroform is not inflammable, it is possible to run the oil extractors during the night, while we are absent from the laboratory, and it would appear from the results found by this committee that chloroform removes some fatty materials which are not removed by other solvents.

WRIGHT: Regarding the substitution of chloroform for petrolic ether, I hesitate somewhat in recommending this substitute. In the first place chloroform is more expensive than petrolic ether. If petrolic ether does not give the correct results, we want something that will, but to have it generally adopted, we must choose an inexpensive solvent. My results bear out the results of the three members whose average analyses you submitted to me, in that chloroform extracts more from leather than does petrolic ether, but the question has arisen in my mind whether it does not extract something other than fat. Petrolic ether extracts all matter that acts as a lubricant in the leather, and I do not know whether the other matter extracted by chloroform should be classed under the heading of fat.

I am non-committal as regards adoption of chloroform as an efficient solvent. I believe that further committee work should be done, working only with petrolic ether and chloroform to determine just what is extracted by chloroform that is not extracted by petrol. In view of the fact that there is not sufficient time to do this work before the committee report is rendered, it would be advisable in my opinion to continue the work next year. I do not believe that the official methods should be changed without some exhaustive work being done on this subject. The results obtained by the committee are a very valuable start in this direction and the data obtained is of great value.

ROGERS: The results which you sent show that chloroform extracts more material than the other solvents. Inasmuch, however, as it is not known exactly how much fat was added to the leathers, it is impossible to determine whether any one of the solvents tested gives 100 per cent. actual efficiency, the efficiency mentioned in your recent table being only a comparison between the solvents.

I am willing to vote for the use of chloroform as a provisional solvent for fats, while further investigations are being conducted to determine the actual efficiency of different solvents in the extraction of fats.

KERN: I favor the adoption of chloroform as the official solvent for the reasons given in the chairman's recommendation.

ATTEMPTS TO DETERMINE THE ABSOLUTE EFFICIENCY OF A SOLVENT.

Although chloroform has shown the greatest relative efficiency of the several solvents examined, it is still possible that even this solvent does not extract all of the added fat. Churchill has suggested a method by which the absolute efficiency of a solvent can be determined provided we can determine the percentage of hide substance in each of the samples numbered from 1 to 12 with extreme accuracy. Taking the principle of Churchill's method as a basis, the chairman has worked out the following details:

Let a equal parts of hide substance per 100 parts of unstuffed leather.

b equal parts of hide substance per 100 parts of stuffed leather.

f equal parts of fat added per 100 parts hide substance.

To 100 parts of unstuffed leather we add $fa/100$ parts of fat.

We then have a parts of hide substance per $100 + fa/100$ parts of stuffed leather.

This equals $10{,}000a/(10{,}000 + fa)$ parts of hide substance per 100 parts of stuffed leather, but this equals b.

Therefore $f = 10{,}000\ (a - b)/ab$.

The only drawback in the matter of applying this formula to the committee results is that the accuracy of the hide substance

determinations cannot be guaranteed to the required degree. The chairman is of the opinion that the averages of these determinations are probably accurate to 0.5 per cent. This makes an extreme difference in the value for $a - b$ of 2.0 per cent. Even allowing for such a big variation, it is of some value to make the calculations.

In Table XVII are given the values for f actually found for the different solvents, along with the limits for f calculated from the above formula on the assumption that the hide substance values are accurate to 0.5 per cent. Where the experimental value lies between these calculated limits, no conclusions can be drawn as to whether the value found is high or low. On the other hand, when the experimental value lies outside of the calculated limits, we can tell whether it is high or low, *provided* we can guarantee our hide substance figures to 0.5 per cent. That we can do this is, of course, only an opinion.

In the cases of three sets of leathers, no conclusions can be drawn at all. In the other three, petrol appears unmistakably low. The results for samples No. 9 and No. 10 suggest that in the case of sulphonated oils, none of the solvents extracts all of the added fat, although chloroform is very much more efficient in this respect than any other solvent. In the case of leathers No. 11 and No. 12, the fact that the chloroform value is so near the lowest calculated value suggests that probably here too no solvent is extracting all of the added fat.

Referring to leathers No. 11 and No. 12, Churchill says: "If my figures for hide substance are correct, it would seem that none of the solvents are taking out the entire amount of added grease. I believe that we can have such conditions in which the highly oxidized fats would be almost impossible to extract from leather. I have an interesting sample of some grease that contained 'blown cottonseed oil.' Some portions of this material are almost impossible to dissolve even in boiling alcohol and yet would have to be considered as fats."

Another method of determining the absolute efficiency of a solvent is the one which led Wilson and Kern to suspect that petrol is not capable of dissolving certain types of fats which may be present in leathers to very appreciable extents. While

TABLE XVII.

Sample numbers	Increase, due to stuffing, of parts of fats per 100 parts hide substance						Conclusions drawn
	Calculated limits between which true value lies	Value found using					
		Petrol	Carbon disulphide	Carbon tetrachloride	Ethyl ether	Chloroform	
1 and 2	23.77 and 31.17	22.28	23.75	24.50	25.93	26.11	Petrol is not extracting all of the fat.
3 and 4	6.35 and 9.80	8.29	8.49	8.75	8.51	8.97	Inconclusive.
5 and 6	71.66 and 79.59	74.49	75.74	75.84	76.89	77.10	Inconclusive.
7 and 8	18.89 and 25.97	20.61	22.17	22.47	23.67	23.66	Inconclusive.
9 and 10	8.72 and 11.57	5.31	6.55	7.75	6.63	8.22	No solvent is extracting all of the fat, but chloroform is very much more efficient than any other.
11 and 12	64.54 and 73.51	62.11	63.24	63.61	64.97	65.23	No solvent, excepting chloroform and ethyl ether, is extracting all of the fat.

investigating the changes taking place in samples of leather during the various processes, they found that fat liquoring with oxidized fats seemed to cause an increase in the degree of tannage of certain vegetable leathers under conditions such that there could be no increase in the percentage of fixed tannins. The question arose as to whether or not an oil tannage resulted from the use of oxidized oils, but when ethyl ether was used as the solvent both before and after fat liquoring, no change in the degree of tannage could be detected. The conclusion was that the petrol was not dissolving the oxidized fats or fatty acids.

TABLE XVIII.

Showing changes in the degree of tannage due to stuffing.

Sample	Solvent used in making fat extraction				
	Petro	Carbon disulphide	Carbon tetrachloride	Ethyl ether	Chloroform
Leather No. 2 after fat liquoring	62.60	60.26	60.14	58.30	58.49
Leather No. 1 before fat liquoring	59.48	59.19	59.01	58.37	58.30
Difference	3.12	1.07	1.13	—0.07	0.19
Leather No. 8 after stuffing	57.62	56.07	56.05	54.28	54.81
Leather No. 7 before stuffing........	55.18	55.13	55.04	54.35	54.91
Difference	2.44	0.94	1.01	—0.07	—0.10

(The figures indicate that chloroform and ethyl ether are extracting practically all of the added fats; carbon disulphide and carbon tetrachloride are appreciably less efficient, while petrol is much less efficient.)

The committee results for the two pure vegetable leathers also bear out this conclusion. The percentage of fixed tannins is calculated by subtracting from 100 the sum of the percentages of water, fat, hide substance, matter soluble in water, and insoluble ash. The degree of tannage is taken as the parts of fixed tannins per 100 parts of hide substance. These values are given in Table XVIII. It may be argued in this case also that the determinations are not sufficiently accurate to warrant our drawing any conclusion. Our reply would be that wherever we have tried out the method, we found a greater degree of tannage after fat

liquoring than before when using petrol as the solvent, but found little or no change when using ethyl ether or chloroform.

CHAIRMAN'S COMMENTS.

When the question of adopting chloroform as the official solvent for the determination of fat in leather is put to a vote, the members of the Association will naturally want to know as much as possible concerning the matters other than fat which chloroform dissolves from leathers. Several committee members have demonstrated that chloroform removes at least traces of tannins from some leathers. The problem is largely one of determining whether the error due to the dissolving of matter other than fat by chloroform is greater or less than the error due to incomplete solution of the fats when petrol is used.

Orthmann insists that the question be settled by a direct analysis of the chloroform extracts, and we should agree with him, if any method were known by which the extracts from all kinds of leathers could be analyzed sufficiently accurately for the purpose. As mentioned before, the difficulty seems to lie in finding a method for making a quantitative separation of all the different kinds of oxidized fatty acids from all organic matter other than fats or fatty acids which might be present in the extract. Until such method is brought forward, his insistence must go unheeded. His contention regarding the formation of compounds of chrome and fatty matter which are soluble in chloroform is easily tested by ashing the extracted matter and determining the chrome content. Kern has done this for numbers of chrome leathers, finished and unfinished, and finds only negligible amounts of chrome present and usually as much in the petrol as in the chloroform extract. The ash contents of the chloroform extracts are generally higher than those of the petrol, but these differences are small compared to the differences in fat content found. Orthmann seems to have missed the principle involved in the committee procedure when he says: "You base the efficiency of chloroform upon the sole fact that it extracts more matter than any of the other solvents tried by the committee." Quite on the contrary, we have ignored the results for leathers No. 13, No. 14, and No. 15 in all our arguments and have dealt only with the matter which a given solvent extracts from a fat liquored leather *in excess* of that which it extracts from the same leather before fat liquoring, which distinction is vital.

That the quantitative analysis of the chloroform extracts is no very simple procedure is also indicated by the fact that no committee member reported having even attempted it, although all were requested to do what they could in this direction. On the other hand, the indirect methods employed in the committee work have given evidence that, in the case of the first twelve leathers, the amount of matter other than fat extracted by chloroform is negligible compared to the amount of fatty matters not extracted by petrol. If our original assumptions are correct, the error due to using chloroform cannot exceed the difference between the chloroform and petrol values for per cent. of fat in the unfat-liquored halves of the leather. Reference to Table XVI will show that this is generally much smaller than the difference between the chloroform and petrol values for per cent. of fat in the fat liquored halves.

The only remaining argument against accepting chloroform as the most efficient solvent for the first twelve leathers is that it is conceivable that a non-fatty constituent of an unfat-liquored leather which is insoluble in chloroform may become so altered by the addition of fat liquor as to be rendered soluble in chloroform to such an extent as to cause appreciable errors. This simply raises the question as to the validity of our original assumptions. In the case of leather No. 10, it seems to us that the fat liquor could have no such action upon anything but the chrome, and Kern has shown that the chrome content of the chloroform extract of this leather is of negligible magnitude. Yet petrol shows less efficiency with this than with any other leather examined. Here we have evidence against the argument for at least one type of leather, with no evidence in its favor. In addition, the data given in the preceding section, so far as it tells anything, strengthens the view that whatever error may be involved in the use of chloroform, it is less than that caused by the use of petrol.

Wright has taken a non-committal stand which has to commend it the several points which he raises. But if we are to make progress, we must at all times be prepared, in matters which we do not completely understand, to estimate the proportionality between probable right and probable wrong and to act upon our findings, which in this case favor the change from petrol to chloroform.

Since the majority of the committee has voted in favor of proposing to the Association that chloroform replace petrol as the official solvent until such time as a better solvent is found, the chairman will submit the proposal in suitable form through the proper channels.

The committee results for water soluble matter show wide discrepancies between the several laboratories. This subject is, therefore, in line for investigation, but it ought to be taken up as a part of the greater scheme of complete leather analysis rather than as an independent problem.

One of the unsatisfactory features of committee work of this kind is that it deals with only one phase of a greater subject, all parts of which should be considered in relation to one another. It will probably eventually be found necessary to establish one or more permanent committees to sit upon the whole question of leather analysis and co-ordinate the work of sub-committees dealing with individual determinations. Wright doubts whether any matter should be classed as fat which does not lubricate the leather, Rogers would not include soap, and Orthmann points out the danger of including rubber, resins, and sulphur. Against these we have the man to whom the degree of tannage means more than the fat content, but he cannot get this without first knowing the fat content, and if soaps, resins, sulphur, and dyes are not extracted or determined in any other way, he would prefer to have these things included in the fat determination in order that he might get a more accurate estimate of the amount of fixed tannins in the leather. Veitch gives reasons why it may be found advisable to keep the analysis of sole leather distinct from that of upper leather. Still another question arises in the matter of from what part of a hide the sample for analysis shall be taken. Knowing the fat content of the shanks or shoulder will not always give one information concerning the fat content of the butt, or of the hide taken as a whole. Our methods for leather analysis are so comparatively meager and the possible viewpoints so many that an almost endless argument could be carried on, if the question of the determination of fat were discussed aside from the question of leather analysis as a whole.

LEATHER AND GLUE.*

By Joseph T. Wood, F. I. C.

In the tanning industries the quantity of work, both in research and investigation of processes, continues to suffer from the war.

The younger men in the two British centers, London and Leeds, are serving in the army, and the chemists who have remained behind in the works and laboratories have had their attention confined principally to problems connected with the rapid production of leather for army use, and have had neither time nor inclination to read papers or publish new work.

The principals have been consulted by the War Department, and have rendered valuable aid by their advice in technical matters. The results achieved have surpassed expectation, and both the British Army, and many of the Allied troops, have been supplied with boots and equipment of better quality than in any previous war.

Mention should also be made of the vast quantities of sheep leather which have been turned out for jerkins for the winter, and for aviators' clothing and gloves.

Preparatory Processes.

Preservation and Disinfection of Hides and Skins.—Joint regulations[1] have been drawn up by the Secretary of Agriculture and the Secretary of the United States, governing the certification and disinfection of hides, fleshings, hide cuttings, etc., for entry into the United States. The circular of the Treasury Department (T. D. 36,754)[2] contains these regulations, which took effect on January 1, 1917.

A. Seymour-Jones[3] continues his work on the sterilization and curing of dried hides, especially with reference to anthrax. He states that the Schattenfroh process of sterilization (see Annual

* Reprinted from the Annual Reports of the Society of Chemical Industry on the Progress of Applied Chemistry. (In this article all references marked *J.* refer to the *Journal of the Society of Chemical Industry.*)

[1] *J.*, 1917, 39; this Journal, 13, 47.

[2] Reprinted in the *Board of Trade Journal*, Dec. 21, 1916, 884-887.

[3] This Journal, 1917, 68; *Coll.* (London), 1917, 121.

Report, Vol. 1, p. 227) damages the fibers of the skin, and moreover would not be practicable in the hands of ignorant natives. The efficiency of the formic-mercury process has been proved in practice, and it is suggested that the Governments concerned should forbid the importation of hides and skins unless (1) they have been submitted to the ordinary "wet-salting" process immediately after flaying; or (2) if cured by drying they have been converted back to the "wet-salted" state by the formic-mercury process before leaving the country of export.

A. Eichhorn, W. N. Berg, and R. A. Kelser[4] publish immunity studies on anthrax serum, and give results of methods for its examinations, and also the results of experiments on animals. In many cases death was prevented.

The meeting of the A. L. C. A. in June, 1917,[5] at Atlantic City, was devoted to the discussion of anthrax. The following papers were read: "Anthrax," A. S. Ross; "Practice and Theory of Treatment and Diagnosis of Anthrax," H. J. Frisbie; "The Nature of Anthrax and Anti-Anthrax Serum," A. Parker Hitchens; "Anthrax and Hide Disinfection," Van A. Wallin; "Discussion on Anthrax," R. W. Hickman and others.

The practice of bringing together a number of experts on the same subject is an excellent one, and brings to light matters which otherwise would remain hidden from the general public. Our own societies might take pattern by it.

Useful directions for the treatment of anthrax are given by C. R. Oberfell.[6]

At the same meeting A. Seymour-Jones read a paper on the future of hide supply, pressing for the improved preservation of hides imported from foreign countries. There is no doubt that skins preserved as he suggests (by the formic mercury process) would be better for the tanner, and the risk of infection by anthrax would be avoided. It does not appear that much can be done until the Governments of the chief importing countries come to an agreement on the matter, and make the system of preservation compulsory.

[4] *J. Agric. Res.*, 1917, 8, 37; *J.*, 1917, 302.
[5] This JOURNAL, August, 1917.
[6] This JOURNAL, 1917, 51.

A paper by R. M. Chapin[7] on the chemical composition of lime-sulphur animal dips is of interest to leather manufacturers on account of the explanation given of the reactions which take place in the preparation of lime-sulphur solutions used in unhairing.

Puering and Bating.—J. Meister[8] patents the use of pepsin for the deliming and bating of skins. These are submitted to the action of pepsin in very dilute hydrochloric acid, the temperature being maintained at 40° C., and other acids (boric, lactic) and also salts (ammonium chloride) are added to keep up the hydrion concentration. In view of the fact that pepsin acts in acid solution of a concentration equal to 0.2 per cent. hydrochloric acid, it is quite certain that the skins would be swollen to such an extent as to render them useless for tanning.

A new antiseptic, "mercurophen" (sodium oxymercuri-o-nitrophen-oxide), is described by J. F. Schamberg, J. A. Kolmer and G. W. Raizin.[9] By the Rideal-Walker test it exhibits 10,000 times greater germicidal power than phenol, against B. typhosus, and over 30 times greater activity than mercuric chloride. It is suggested by a writer in the *Leather World,* that this antiseptic might be of use for the disinfection of hides and skins in a similar way to the use of mercuric chloride in the Seymour-Jones formic-mercury process.

Pickling.—Restrictions in the supply of sulphuric acid have led to the trial of niter cake as a substitute for acid in the pickling process. The cake contains from 26 to 30 per cent. of sulphuric acid, and a solution to which is added the proper quantity of common salt may be used for pickling. The storing and solution of the cake present some difficulties, and its use requires control from the laboratory.[10]

E. Nihoul[11] gives an account of the commercial manufacture

[7] U. S. Dept. Agric., Bull. No. 451, 1916; *J.*, 1917, 232; abstracted this JOURNAL, 13, 38.

[8] Fr. Pat. 480,196, 1915; *J.*, 1917, 151.

[9] *J. Amer. Med. Assoc.*, 1917, 1458; *J.*, 1917, 733.

[10] For a discussion on the subject and references to previous papers, see *J.*, 1917, 1216.

[11] "Apropos des acides lactiques et butyriques." *Coll.* (London), 1916, 242.

of lactic and butyric acids, together with methods of analysis. There is no doubt that after the war the use of these acids in the various preparatory processes will be largely increased.

Tanning.

Vegetable Tannage.—N. Flamel[12] gives a useful general review of the various processes proposed from 1764 to the present time for lessening the time of tannage in the production of leather. The general conclusion arrived at is that leather rapidly tanned, by means of vegetable tanning materials, is not equal in quality to leather tanned by the slow process. Rapidly tanned leathers in general contain a larger percentage of water-soluble material than those more slowly tanned, although this difference is not distinctive.

A valuable paper on drum tannage, containing many practical wrinkles, by Oskar Reithof,[13] includes a table showing the degree of tannage, and per cent. of hide substance in different standard tannages. When properly controlled the tensile strength of drum or tumbler-tanned leather is fully equal to that of pit-tanned leather. Procter also has shown that a very high percentage of combined tannin (degree of tannage) actually reduces the breaking resistance.

F. A. Coombs[14] gives an account of comparative sole leather tests with Australian pine barks (see Ann. Rep., Vol. 1, 1916, p. 240) and a comparison of these with wattle barks. These experiments were carried out on one hide, the butt of which was cut into eight pieces, a diagram of the method of cutting the hide being given. The results show a higher leather return for the pine bark tannage, probably due to the higher acidity of the pine liquors. The leather also resisted water penetration better than the wattle bark leather. The author suggests the drawing up of a standard experimental process for tanning heavy leathers based on these trials. He considers that such a process must be a miniature reproduction of the commercial process.

F. A. Coombs, F. Alcock, and A. Stelling[15] have also given

[12] *Rev. Gen. des Sciences*, 1916, 720; this Journal, 1917, 142.
[13] This Journal, 1917, 322; *J.*, 1917, 931.
[14] *Coll.* (London), 1916, 205; *J.*, 1916, 1028; this Journal, 11, 573.
[15] *J.*, 1917, 188; this Journal, 13, 158.

some useful comparative tests on similar lines with mangrove and wattle barks.

Reithof[16] publishes a series of useful tables showing the relation between specific gravity, per cent. total solids, and tannins, in chestnut extracts and hemlock bark extracts.

M. C. Lamb[17] discusses the causes of the deterioration of leather used in gas meters, and gives specifications for the manufacture of suitable leathers for this work from E. I. Persians, semi-chrome tanned, and pure chrome tanned sheep or lambskins.

E. Nihoul[18] gives a list of eight different tanning materials found in the Belgian Congo. The tannin content varies from 12 to 28 per cent.; he considers that some of these could be economically used in Europe, especially if dry extracts of them were made in the Congo.

Other useful information with regard to vegetable tanning materials is given in the following papers:

Quebracho Extract Manufacture in Argentina and Paraguay. *Board of Trade J.*, Feb. 15, 1917; *J.*, 1917, 226.

Tanning Materials from British Malaya. *Chamber of Comm. J.*, March, 1917; *J.*, 1917, 347.

Indian Sumac. *Bull. Imp. Inst.*, 1916, 14, 482; *Coll.* (Lond.), 1917, 2.

Indian Sumac. Puran Singh, *Ind. Forest Bull.* No. 31, 1916; *J*, 1917, 39.

The Wattle Bark Industry of Natal. *Bull. Imp. Inst.*, 14, No. 4, 599; *J.*, 1917, 558.

"Tarwad" Bark as a Tanning Agent. D. B. Limaye, *Coll.* (Lond.), 1917, 126; abstracted this JOURNAL, 12, 286. (A very full account. This bark, Cassia auriculata, along with babul and myrobalans, form the chief tanning materials used in the tanning of East India skins.) *J.*, 1917, 513.

Babul Pods as Tanning Material. *Bull. Imp. Inst.*, 1916, 14, 612; *J.*, 1917, 559; abstracted this JOURNAL, 11, 539.

Indian Forest Products. R. S. Pearson, lecture at the Soc. of Arts. *J.*, 1917, 631.

Philippine Tanbarks. V. Q. Gana, *Philipp. J. Sci.*, 1916, 11, 231; *J.*, 1917, 1106; this JOURNAL, 11, 233.

[16] *Coll.* (London), 1915, 232; this JOURNAL, 11, 425.

[17] *Coll.* (London), 1916, 248; *J.*, 1916, 989; this JOURNAL, 11, 611.

[18] Note sur quelques matieres tannantes du Congo Belge; possibilite de leur utilization en vue de la fabrication d'extraits sec. *Coll.* (London), 1916, 257.

Liquors from the sulphite-cellulose process of wood pulp manufacture are put on the market under various names, such as "spruce extract," the tanning properties of which are doubtful, but which act as filling materials. In some cases they are used to adulterate genuine tanning extracts. The process of manufacture of wood pulp is described in a paper by Allan Smith.[19]

The detection of wood pulp in extracts and leather is dealt with by W. Appelius and R. Schmidt, *Ledertech. Rundschau*, 1914, 29; abstract in *Coll.* (Lond.), 1916, 288; abstracted this JOURNAL, 9, 566.

J. Paessler[20] has examined the tannin content of green walnut shells. They contain 22 per cent. of a tannin which, though sensitive, is usable. He recommends the collection of these shells for leather manufacture.

A. Seymour-Jones[21] outlines a process for the rapid tanning of sole leather. Instead of removing lime by the suspenders, it is either neutralized or removed by sodium hyposulphite. The hides are then immersed in a neat extract; the tanning will be completed in about 10 days to a fortnight, after which the hides should be laid away in a strong but diluted liquor. In this way the whole operation of tanning may be completed within three weeks.

Neradol.—Patents still continue to be taken out for tanning substances resembling neradol. The Deutsch-Koloniale Gerb. u. Farbstoff Ges.[22] patents the manufacture of tanning substances obtained by the action of formaldehyde, or a substance capable of yielding formaldehyde, on aminonaphtholsulphonic acids or dihydroxynaphthalenesulphonic acids as such, or in the form of their salts in aqueous or slightly acid solution.

The Society of Chemical Industry in Basle[23] patents the use of soluble aromatic compounds containing two or more sulphamino groups, together with a sulphonic group, but no hydroxyl or free amino groups. The leather produced is not colored, and is very similar to vegetable-tanned leather.

[19] *J.*, 1916, 281.

[20] *Ledertech. Rundschau*, 1916, 8, 189; *J.*, 1917, 605.

[21] *J. Soc. Leather Tr. Chem.*, 1917, 2.

[22] Eng. Pat. 18,174, 1915; *J.*, 1917, 93.

[23] Ger. Pat. 297,187; *J.*, 1917, 855.

G. Calvert[24] patents a tanning agent obtained by the interaction of a phenolic substance and formaldehyde in the presence of soap. Since reaction is carried out in the cold it seems doubtful if substances of the type of neradol are formed, in which case the tannage would be a formaldehyde tannage.

Mineral Tanning.—E. Nihoul[25] publishes a comprehensive review of the alum tannage, which is of both theoretical and practical value; although the use of alum in tawing is of very great antiquity, the theory of the process has not been studied so thoroughly as that of chrome tanning.

O. Röhm[26] patents a process for tanning with salts of iron in combination with tannin, a phenol, and an aromatic carboxylic acid. In a further patent[27] the salts of iron are applied in conjunction with formaldehyde. It certainly seems an anomaly that an enemy country is enabled to take out patents here which in many cases are merely "blocking" patents and have never been worked out on a practical scale. A number of patents of this description are being taken out for the application of synthetic products on the same lines as neradol.

P. Kauschke[28] patents a process for the preparation of chrome liquors containing complex organic chromium salts. Chromic acid is reduced in concentrated sulphuric acid solution by means of waste materials containing protein, waste chrome leather, scrap cuttings or parings, reaction being started either by heating or by adding dehydrating or easily oxidizable substances or substances capable of generating nascent hydrogen.

M. C. Lamb and A. Harvey,[29] in a paper on the "Estimation of Chromic Oxide in Chrome Leather," state that a properly tanned chrome leather should contain a minimum of 3 per cent. Cr_2O_3. They also point out that the fat should be extracted from the leather before the analysis is made.

Oil Tannages.—A. Chaston Chapman[30] publishes a very inter-

[24] Eng. Pat. 108,262, 1916; *J.*, 1917, 1019.
[25] *Coll.* (London), 1916, 178; *J.*, 1917, 69.
[26] Eng. Pat. 103,295.
[27] Eng. Pat. 103,827; *J.*, 1918, 14A.
[28] Ger. Pat. 295,518, 1914; *J.*, 1917, 298.
[29] *Coll.* (London), 1916, 201; *J.*, 1916, 1028.
[30] *Chem. Soc. Trans.*, 1917, 111, 56; *Analyst*, 1917, 42, 161; *J.*, 1917, 392, 602.

esting and valuable research on the occurrence in certain fish oils of high percentages of hydrocarbons. In some fish oils very considerable quantities of unsaponifiable hydrocarbons, with very high iodine values, occur. Unless all the constants of such oils are determined, this might lead to the assumption that the oil was adulterated with a mineral oil. Chapman has given the name "spinacene" to this hitherto unknown hydrocarbon, and gives full details of its properties. A point of great importance to the analyst is that it would appear to be difficult to express a definite opinion as to whether a given sample consists of shark liver oil or not.

Finishing Processes.—M. C. Lamb and A. Harvey[31] have examined a large number of animal and vegetable products used in the finishing of leather, and suggest certain standards of quality for these products. Results are given for blood albumen, Irish moss, algin, gum tragacanth (Astragalus gumifera), gum acacia, gum tragasol, and casein.

T. E. Durrant[32] gives an account of "grains" on leather useful for the identification of different skins in printed condition.

Sulphonated Oils.—The use of these oils for fat-liquoring has further increased during the past year, but owing to the increasing scarcity of castor oil a variety of other oils have been used which in many cases have not given such good results as sulphonated castor oil. Further increasing adulteration with mineral oils and ammonia soaps has caused tanners and finishers to pay more attention to the analysis of these oils. This has been the case especially in America, where very valuable work has been done by a committee of the A. L. C. A. under the chairmanship of W. K. Alsop.[33]

One of the points brought out is that there is no well recognized method of determining the source of the oil from which sulphonated oil has been made. If a mixture of oils be sulphonated, including an easily sulphonated oil, such as castor oil, and one more difficult to sulphonate, and then the neutral oils separated, and their constants determined, the presence of castor oils is not apparent, but that of the other oils is, and wrong con-

[31] *J. Soc. Dyers and Colorists,* 1917, 33, 19; *J.,* 1917, 212.
[32] *Leather World,* Dec. 4, 1916; Jan. 11, 1917.
[33] This JOURNAL, 1917, 266, 440.

clusions would be drawn from such results. Alsop's report of the 1917 Committee for the Analysis of Sulphonated Oils should be in the hands of all chemists interested in this work.

R. Hart, in a paper on the Analysis of Sulphonated Oils, reaches the following conclusions: Turkey red oils and similar products are completely saponified by N/2 alcoholic sodium hydroxide. Alkali combined as soap can be determined by titrating its solution with acid in presence of methyl orange. It is feasible to calculate the combined SO_4 from the increase of acidity due to the splitting of the sulpho group. Based on these fundamental points a rapid method has been developed whereby sulphonated oils can be analyzed for fat, ammonia and caustic soda bound as soap, and for sulphuric anhydride in the form sulpho-ricinoleic acid.

Quite recently L. G. Radcliffe and S. Medofski[34] have published work on the sulphonation of fixed oils, with special reference to the textile and leather industries. This paper contains an account of the discovery and constitution of the "Turkey red oils," together with details of the experimental work carried out by the authors to determine the constants of the fatty acids resulting from the saponification of the sulphonated oils. Data are given of sesame, cotton seed, and olive oils, which appear to show that the most easily sulphonated oils are those containing olein or oleic acid, and that the products of the reaction after saponification contain lactones and hydroxy-acids. The tables given are too extensive to be quoted here. The whole paper is a very valuable contribution to the constitution of sulphonated oils.

R. Kobert and W. Greuel[35] state that indications of the strength and action of commercial Turkey red oils ("Solvines") can be obtained from experiments with blood corpuscles. On the results of their work they propose a method for the biological valuation of these oils; among other things it is suggested that saponins could be used as substitutes for Turkey red oil in the tanning industry.

O. Röhm[36] patents the use of castor oil sulphonated just sufficiently to remain soluble after neutralization.

[34] *J. Soc. Dyers and Col.*, 1918, 34, 22; *J.*, 1918, 157A.
[35] *Coll.*, 1916, 261; *J.*, 1917, 91.
[36] Eng. Pat. 103,668; *J.*, 1917, 1141.

T. Sandland[37] patents a composition for finishing and dressing leather for furniture. It consists of 3 parts of each hard drying elastic varnish, methylated spirit, and petroleum, 1 part of boiled linseed oil, and 6 parts of benzine or benzol. Pigments may be added as desired. The composition may also be used for the renovation of old and worn leathers.

Waste Products.—America still leads the way in the study of the economical disposal of tannery wastes and sewage. D. D. Jackson and A. M. Buswell[38] investigated the subject from the point of view of prevention of anthrax infection of cattle due to the presence of anthrax bacilli in the tannery effluent. In the course of their investigations they obtained valuable information on the value of various disinfectants, sulphur dioxide, calcium hypochlorite, and chlorine. In a discussion on the above paper it was stated that 50 parts of chlorine per 1,000,000 killed anthrax spores suspended in the general effluent of the tannery. Liquid chlorine was found to be much more efficient than bleaching powder. The amount of chlorine used was sufficient to combine with all the organic matters, so that no free chlorine was found in the effluent.

H. B. Hommon[39] gives details of sewage disposal plants at a tannery of sole leather in Virginia, and at a harness leather tannery at Cincinnati, Ohio, and also particulars as to the disposal of the sludge. The following tables given in the paper are of general interest:

ANALYSES OF THE RAW AND TREATED WASTES AT THE TANNERY OF THE DEFORD LEATHER COMPANY, LURAY, VA.

Source	Susp. solids	Organic and free ammonia	Nitrites	Nitrates	Oxygen consumed 30' at 96° C.
Beam house	850	—	—	—	600
Hair wash	900	—	—	—	200
Spent tan liquor	1,100	—	—	—	13,000
Composite	1,200	70	—	—	900
Effluent set. tank	450	55	—	—	530
Effluent cinder filter	160	30	0.29	6.0	205
Effluent sand filter	30	25	0.17	23.0	55

[37] Eng. Pat. 17,702, 1915; *J.*, 1917, 93.

[38] This JOURNAL, 1917, 56, 229; *J.*, 1917, 895, 931.

[39] This JOURNAL, 1917, 307; *J.*, 1917, 931.

ANALYSES OF RAW AND TREATED WASTES AT THE HAFFNER BROS. TANNERY, CINCINNATI, OHIO.

Source	Susp. solids	Organic and free ammonia	Nitrites	Nitrates	Oxygen consumed 30′ at 96° C.
Beam house	1,450	100	—	—	800
Spent tan liquor	900	60	—	—	3,900
Composite	1,430	100	—	—	1,000
Effluent set. tank	380	75	—	—	700
Effluent cinder filter	120	30	—	—	300
Effluent sand filter	15	13	0.4	10	85

TABLE SHOWING THE NUMBER OF GALLONS OF WASTE DISCHARGED PER DAY AND PER HIDE FROM THE DIFFERENT SOURCES AT THE TWO TANNERIES.

	Deford Leather Co., Luray, Va. Gallons		Haffner Brothers, Cincinnati, Ohio Gallons	
Type of waste	Per day	Per hide	Per day	Per hide
Beam house	65,500	240	52,700	316
Hair wash	23,500	85	Do not wash hair	
Spent tan	14,000	51	2,800	17
Total	103,000	376	55,500	333

E. Ardern[40] gives an account of experiments made for the Rivers Committee of the Manchester Corporation on the activated sludge process of sewage purification, in which he shows that, contrary to the opinion formed as the result of earlier experiments when working with a strong sludge sewage, the maintenance of the activity of the sludge is not dependent on the stage to which nitrification is carried. It would appear that the cost of dewatering and drying the sludge will be more than repaid by the value of the resultant dry sludge.

A. Harvey[41] gives a concise account of the methods used for the analysis of tannery wastes for use as manures at the South-eastern Agricultural College, Wyoming.

A further paper on the treatment of tannery sewage by C. L. Peck[42] gives a summary of results obtained in May, 1917, by the Dorr method of sedimentation.

M. C. Lamb[43] has brought together various proposals and

[40] *J.*, 1917, 65. See Report, 1916, 237.
[41] *Coll.* (London), 1916, 151.
[42] This JOURNAL, 1917, 422.
[43] *J.*, 1917, 986.

methods for the utilization of condemned army boots. One of the proposals is to cut the leather into small pieces, which are then mixed with asphalt, bitumen, and limestone, and used for laying the surface of roads (patent by S. Brough of Handsworth, 1910). Such a road is more resilient and noiseless than the ordinary macadam road. The Roads Board are now interesting themselves in the matter, and it is probable that the process will be introduced into practice. From a chemical point of view, dry distillation of the leather is of greater interest, and promises good commercial results. The following products were obtained from the dry distillation of 1 ton of condemned boots (500 pairs), prices based on market values October, 1917: 560 pounds purified charcoal, value £10; 515 pounds ammonium sulphate, value £4, 2s. 9d.; 67 pounds of grease, value £1, 10s.; and 425 pounds metal, value 19s., a total of £16, 11s. 9d., which should leave a good margin of profit. Several other methods of utilizing old boots are given in Lamb's paper.

Machinery.—Owing to control of all engineering works by the Ministry of Munitions, it has been extremely difficult for engineers to turn out new machinery, or to keep the trade supplied with its normal requirements. The Committee on "Trade after the War," of which Sir Henry Ledgard is chairman, have met the trade engineers, and are endeavoring to work out a scheme so that they may be able to produce all the machinery required for the leather trade in this country. It seems probable that this can be done by the firms producing tanners' machinery combining instead of competing amongst themselves.

Analytical Methods and Chemistry.

There has been no striking advance in the chemistry of tannins, or in new analytical methods, since the last report was written, but a good deal of steady, useful work has been done on present methods.

D. McCandlish and J. A. Wilson[44] reply to the criticisms of H. G. Bennett on their method for the determination of alkaline sulphides in lime liquors. The problem of determining accurately the amount of sulphide in lime liquor has never been solved to the satisfaction of all concerned.

[44] This Journal, 11, Dec., 1916; *Coll.* (London), 1917, 10; *J.*, 1917, 93.

Bennett[45] continues the discussion on McCandlish and Wilson's method (see Ann. Rep., 1916, 1, 229). He points out that the stronger the limes are in sulphide, the weaker they are in lime, hence in such liquors the tendency of hydrogen sulphide to escape is greater.

For very small quantities of sulphides, the method of W. A. Drushel and E. M. Elston[46] is suitable. This is a colorimetric method based on the liberation of hydrogen sulphide, which is absorbed by lead acetate paper.

Levi and Orthmann[47] estimate the total sulphur in leather by precipitating as barium sulphate after the organic matter has been destroyed by boiling the leather with a mixture consisting of potassium bichromate 50 grams, water 150 cc., and concentrated hydrochloric acid 50 cc.

H. G. Bennett[48] gives details of methods employed by him for the analysis of limed pelt. In determining the total alkalinity, the hydroxides and sulphydrates of calcium and sodium, ammonia and organic bases, are extracted from the pelt by means of a 3 per cent. solution of boric acid, and are then titrated with standard acid, using methyl orange, which is unaffected by the boric acid and by hydrogen sulphide. Details of the mode of estimation of ammonia, sulphide, soda, lime, hide substance, and salt are given, for which the original paper must be consulted.

H. G. Bennett[49] has determined the amounts of nitrogen in keratin from various sources. No difference was found between the keratin from ox hide of various colors, or of the two sexes, or at different seasons of the year. The mean percentage of nitrogen was 16.3 per cent. Keratin from dog hair (white fox-terrier) contained 17.2 per cent. N; that from goat hair 16.7 per cent. N; from human hair, woman 16.1 per cent. N; man 16.4 per cent. N; from finger nails 16.4 per cent. N.

The American Leather Chemists Association have published their revised official methods for the analysis of vegetable materials containing tannin.

[45] *J. S. L. T. C.*, 1917, 3.
[46] *Amer. J. Sci.*, 1916, 42, 155; *J.*, 1916, 925.
[47] This JOURNAL, 1916, 11, 496; *J.*, 1916, 1071.
[48] *Coll.* (London), 1916, 125; *J.*, 1916, 645.
[49] *Coll.* (London), 1917, 101.

In a very useful review of developments in the analysis of tanning materials, H. G. Bennett[50] discusses the official method of tannin analysis from the point of view of an adsorption phenomenon, detannization with hide powder, being a case of surface action, and subject to the ordinary adsorption law.

As a result of the discussion it is concluded that the hide powder process would be greatly improved in both concordance and accuracy by the adoption of the following modifications—Detannization of infusions of only half the strength now used, *i. e.*, of solutions containing 0.2 per cent. of tannin approximately instead of 0.4 per cent. Neutralization of all acidity of hide powder before chroming, and the employment of the more basic salt $Cr_2Cl_2(OH)_4$ for chroming purposes, thus obtaining a constant acidity of the hide powder, mainly due to non-swelling acids. The standardization of hide powders by the determination of relative specific surface, and the employment of a constant active surface in each analysis. The use of 5 grams of hide powder of the type now in use instead of 6.5 grams. In general, to use that quantity of hide powder, which is approximately 10 per cent. greater than the minimum amount necessary to detannize a 0.45 per cent. solution of gallotannic acid.

As a further result of the discussion,[51] Bennett considers there is little hope of changing the adsorbent, since substances which have been proposed as a substitute, such as oxides of copper, aluminium, lead and nickel, detannize by adsorption rather than by chemical action, so that the errors are much the same as with hide powder.

The testing of hide powder is dealt with in the report of the Hide Powder Committee.[52]

The question of the effect of hard waters on the tanning process has recently received renewed attention in America. It is well known that in laboratory extractions of tanning materials with hard water a sensible loss of tannin occurs. The subject was exhaustively treated by Nihoul and his collaborators in several

[50] This JOURNAL, 1916, 11, 546-570.
[51] *Coll.* (London), 1917, 52, 84.
[52] *Coll.* (London), 1916, 155.

important papers,[53] and his results have recently been confirmed by E. Schell,[54] who finds that the carbonates in the water are the chief cause of the loss. A committee of the A. L. C. A. have now issued their report,[55] giving the result of a series of comparative extractions with distilled water and with various hard waters, in which the conditions were designed so as to be approximately analogous to those prevailing in tannery practice. The general concensus of opinion by the individual members of the committee as to the conclusions to be drawn from the tabulated results, indicates a serious doubt as to any destruction of tannin by hard water as used in practice. It was shown, however, that salt had a detrimental effect in the leaching, and that total solids have more effect than temporary hardness. This may well be, since at the temperatures used the carbon dioxide in the water will be given off and the carbonates precipitated. The color of the infusions from the hard water was darker than the distilled water, and color tests on sheepskin were redder with hard water than with distilled water. In the discussion which followed the reading of the report, Mr. Smoot said that in a certain tannery it was found that 20 per cent. more bark was necessary to tan a given quantity of hides when the leaching was done with hard water than when soft river water was used. It would appear from this that there are still some unknown factors in the problem, which probably differ in each tannery.[56]

The important question of the determination of free sulphuric acid in leather has received attention in America by a committee of the A. L. C. A.,[57] the members of which carried out a series of comparative trials with the Wuensch and Procter-Searle methods. The results indicate that the Wuensch method is unreliable and fails completely in the presence of magnesium sulphate, which has no effect on the Procter-Searle method; the latter, however, does not give reliable results in the presence of iron, aluminium, ammonium, and chromium salts.

[53] *Bull. Assoc. Belge des Chim.*, 1903, 17 (10); 1904, 18, 185, 220; see *J.*, 1901, 1005; 1904, 122, 1155.

[54] *La Halle aux Cuirs*, Aug., 1917; *J.*, 1917, 1243.

[55] This JOURNAL, 1917, 360; *J.*, 1917, 1056.

[56] *L. T. R.*, 1917, Oct. 10.

[57] This JOURNAL, 1917, 344.

A quick and reliable method for the detection of neradol in leather is needed. Unfortunately both neradol and sulphite cellulose give a precipitate with the aniline test (Pocketbook, p. 56). Most of the reactions which have been proposed for the detection of neradol in leather either are not sufficiently sensitive or are interfered with by the presence of other tanning materials. E. Seel and A. Sander[58] give the following method:

Twenty grams of the leather cut into small pieces is boiled with 200 cc. of water for 15/30 minutes. 100 cc. of the hot filtered solution is treated with a mixture of equal parts of 40 per cent. formaldehyde, concentrated hydrochloric acid and water,[59] and boiled for 30 minutes under a reflux condenser. After cooling, the solution is filtered and concentrated and tested as follows:

(*a*) Hydroxyazo Reaction: 5 cc. of the concentrated solution is treated with excess of alkali, cooled with ice, mixed with about half its volume of alcohol, and three or four drops of a solution of diazotized *p*-aminophenol added. A blue coloration indicates the presence of neradol D.

(*b*) Indophenol Reaction: 5 cc. of the above concentrated aqueous extract of the leather is treated with a drop of solution of the hydrochloride of dimethyl-p-phenylenediamine (obtained by reduction of methyl orange). The mixture is made alkaline with caustic soda, and treated with one or two drops of a 5 per cent. solution of potassium ferricyanide. A blue coloration indicates the presence of neradol D.

For the detection and differentiation of vegetable and synthetic tannins, see also Laufmann (*Chem. Zeit.*, 1917, 41, 273; *J.*, 1917, 513; abstracted this JOURNAL, 13, 224, 345).

Physical Chemistry.—Quite a number of important contributions have been made to this division during the past year, the true bearing of which on practical tanning is not yet clear; there is, however, no possible doubt that such work will in the future enable us to make progress far greater and with more safety than

[58] *Z. angew. Chem.*, 1916, 6, 325, 333; *J.*, 1916, 1028.

[59] Stiasny, *J.*, 1906, 275.

in the past. Procter and his pupils have recently shown that much which has been attributed to the surface-action implied in the name "capillary chemistry" is really subject to more general laws, and can be fully explained by mass action, electrochemical attraction, and osmotic pressure.[60]

H. R. Procter has given a general review of the colloid chemistry of tanning in the recently issued Report of the British Association. The review is accompanied by a complete bibliography, which will prove of the greatest use to all chemists, not alone those engaged in tannery practice. The review is a concise account of our knowledge of the tanning process up to date, and should be read and studied in its entirety. Full use of it is made here.

The researches on the swelling of gelatin have been carried on by Procter[61] for a number of years, and have led to very important results which are applicable not only to the processes of tanning, but also to general physiological processes taking place in the living body.

Procter and Wilson (see list of papers 1, 4, 5 and 6; also Report, 1916, 230), in their work on the equilibrium of dilute hydrochloric acid and gelatin, have derived quantitative equations[62] which explain the swelling and contracting actions of electrolytes on colloid jellies, as well as the various effects of adding electrolytes to sols. The derived formula apply to the whole colloid state, and therefore in themselves offer a quantitative explanation of the mechanism of tanning.

Vegetable tannage appears to be of a more colloidal or physical character than alum or chrome tannage. Tannins, like the proteins, appear to form colloidal rather than true ionic solutions, and the particles are negatively charged, passing to the anode in electophoresis. Whether the charge is due to ionization or to the fixation of an electrolyte ion is immaterial for our purpose. The gelatinous fibers take a positive charge in acid and a negative one in alkaline solutions; hence in faintly acid solution, which produces the strongest positive charge they attract and precipitate

[60] "Colloid Chemistry of Tanning." Brit. Assoc. First Report on Colloid Chemistry and Its Industrial Application, 1917, p. 5.

[61] *Chem. Soc. Trans.*, 1914, 105, 313; *J.*, 1914, 326.

[62] *Chem. Soc. Trans.*, 1916, 109, 1327; *J.*, 1917, 92.

the tannin particles, while in alkaline solution no tannage takes place, and in those too strongly acid the tannins themselves are precipitated;[63] in fact, such colloid precipitations, due to electric charges, do not seem to differ in principle from ionic reactions, though, owing to the varying size of the particles, and of their charges they are less definite and quantitative. Whether ultimately any closer combination with the fiber ensues, as is suggested in the case of mineral tannages, remains for the present uncertain, but in long continued tannage there is a further deposition of difficultly soluble matters on and between the fibers by forces generally called "adsorption."

Proteins, among which gelatin must be included, are now known to consist of open or closed chains of amino acids, in which the carboxyl group of one is linked to the amino group of the next with elimination of the elements of water. In closed chains, groups within a single molecule having a terminal amino and carboxyl group, also give rise to similarly united ring structures. In this case the molecule is electrically neutral, and non-reactive till the ring is broken, while the open chains are amphoteric, basic by their terminal amino group, and acid by their carboxyl. A very useful practical distinction is that ring proteins are unattacked by trypsin alone, while pepsin is able to open the ring.

Gelatin can be digested by trypsin, but collagen is only attacked by pepsin, hence the view, supported by other facts, that collagen is the ring or anhydride form of gelatin into which it is converted by continuous boiling or by the action of acids or alkalies.

Procter found that when gelatin is placed in a solution of hydrochloric acid, the maximum swelling, which may reach an absorption of 50 cc. of liquid for 1 gram of dry gelatin, occurs at an acid concentration under 0.005N, from which it rapidly falls in a curve of hyperbolic type as the concentration is increased, the equilibrium being completely reversible up to about 0.25N, beyond which some secondary reaction, probably a further breaking up of the proteid chain, begins to take place. At the same time the total absorption of acid steadily increases with concentration in a curve which may be closely represented by the ordinary adsorption formula: $a=kx^{\frac{1}{p}}$, where a is the total acid, x the

[63] *Chem. Soc. Trans.*, 1916, 109, 1329; *J.*, 1917, 92.

concentration of the external solution, and k and p are constants, but which is really due to a complicated osmotic equilibrium.

Gelatin, being amphoteric, acts as a very weak alkali in presence of hydrochloric acid, and forms a gelatin chloride, which like most salts is highly ionized (in fact to practically the same extent as hydrochloric acid itself). The base, however, is very weak, its ionization being of the same order as that of water, and consequently the salt is largely hydrolyzed, and can only exist in the presence of free acid. This gelatin base, gelatin chloride, and free hydrochloric acid are necessarily present in such a jelly in proportions determined by the concentration of the acid, and instead of a definite point of neutrality such as is given by a strong base, there is only a curve approaching, but never reaching, complete neutralization. This is the explanation of the apparent indefiniteness of protein compounds, which has led many chemists to deny the existence of definite protein salts. By determining the hydrolysis curve and calculating the upper limit to which it tends, it is possible to calculate quite definite combining equivalents. Procter[64] in this way, on the assumption that gelatin had a second valency negligible at low acid concentrations, found a combining weight of 839, while Wilson,[65] from the same experiments, but regarding the apparent second valency as due to incipient decomposition or experimental error, found 768. It is not to be supposed, however, that these comparatively low weights represent the real complexity of the probably polymerized molecule in aqueous solution, but merely the smallest molecular division chemically possible.

J. A. Wilson has published some of the results of his work,[66] which brought about a discussion on theories of leather formation (9) in which the chemical and adsorption theories were criticised from the point of view of the practical tanner. More recently H. G. Bennett,[67] in an able review of the present state of the theory of tanning, gives reasons for pinning his faith to the adsorption theory. He calls attention to the influence of the "lyo-

[64] *Chem. Soc. Trans.*, 1914, 105, 320; *J.*, 1914, 326.

[65] This JOURNAL, 1917, 12, 108.

[66] *J. Amer. Chem. Soc.*, 1916, 38, 1982. See also Nos. 5, 6, and 9 in the list of papers.

[67] *J. S. L. T. C.*, 1917, 130, 169.

trope" series on the operation of tanning. Recent investigations have shown that the physical properties of water are affected by dissolved substances in a definite sequence. For instance, values of the surface tension and viscosity are affected by salts with the same cation in the following order : $CO_3 > SO_4 > Cl > Br > NO_3 > I$. The cations have a similar sequence of effect when salts of the same anion are chosen : $Mg < NH_4 < Li < K < Na < Rb < Cs$.

In this connection E. Stiasny communicated to the writer several years ago a useful table showing the influence of successive series of anions and cations on the various processes involved in tanning. The table is here reproduced in the hope that it may contribute to the fuller understanding of the points to which Bennett[68] has called attention. The direction of the arrows indicates the succession.

Succession of Anions.

$CNS'—I'—Br'—ClO_3'—NO_3—Cl'—C_2H_3O_2'$

$C_4H_4O_6''—C_6H_5O_7'''—PO_4'''—SO_4''$. Increase.

← Swelling of gelatin (by salts).

← Solubility.

← Melting point.

→ Precipitation of + emulsion colloids.

← Precipitation of — emulsion colloids.

→ Increase of speed of ester catalysis (by $H^{\cdot}$) by addition of salts.

← Increase of speed of ester catalysis (by OH') by addition of salts.

← Solubility of CO_2, H_2, H_2S, C_2H_5OH, $CH_3COOC_2H_5$. etc. (by salts).

← Compressibility of salt solutions.

→ Viscosity of salt solutions.

Succession of Cations.

$NH_3'—Ca''—Ba''—Na'—K'$.

→ Swelling and plumping of hides.

← Hair loosening action.

Wilson,[69] in a note on adsorption, calls attention to the fact that

[68] Procter remarks with regard to Bennett's arguments that his statement that colloidal precipitation is electrical and not chemical would be equally applicable to every ionic action.

[69] This JOURNAL, 1917, 126.

if the theory of colloids developed by Procter (v. s.) is correct, it must explain negative as well as positive adsorptions. He considers that it does this.[70]

The following papers on physical chemistry in relation to leather industries may be referred to:

(1) Theory of Vegetable Tanning. H. R. Procter and J. A. Wilson, *Chem. Soc. Trans.*, 1916, 109, 1327; *J.*, 1917, 92; this JOURNAL, 12, 68.
(2) The Equilibrium of Gelatine and Acid. R. Wintgen, *Coll.*, 1916, 301/2; *Coll.* (Lond.), 1917, 43 (abstract).
(3) Swelling of Hides in Presence of Hydrogen Ions. G. Povarnin, *J. Russ. Phys. Chem. Soc.*, 1915, 47, 2064; *Coll.* (Lond.), 1917, 45; abstracted this JOURNAL, 12, 31.
(4) Theory of Colloids. J. A. Wilson, this JOURNAL, 1917, 122; *Coll.* (Lond.), 1917, 97.
(5) Note on Adsorption. J. A. Wilson, this JOURNAL, 1917, 126; *Coll.* (Lond.), 1917, 100.
(6) Theories of Leather Chemistry. J. A. Wilson, this JOURNAL, 1917, 108; *Coll.* (Lond.), 1917, 105.
(7) A Theory of Vegetable Tannin Colloids; Their Constitution and Mode of Action. W. Moeller, *Ledertech. Run.*, 1915; *J.*, 1917, 225; abstracted this JOURNAL, 11, 592.
(8) The Sol and Gel Condition of Gelatin Solutions. L. Arisz, *Koll. Chem. Beihefte*, 7, 1915, Heft 1/3, 1/90; full abstract by Professor H. R. Procter in *J. S. L. T. C.*, 1917, 45; this JOURNAL, 12, 536.
(9) Discussion on Theories of Leather Formation. This JOURNAL, 1917, 450.
(10) Action of Neutral Salts upon Chrome Liquors. J. A. Wilson and E. J. Kern, this JOURNAL, 1917, 445; *J.*, 1917, 1140.
(11) Osmotic Pressure of Gelatin. W. Bilz, G. Bugge and L. Mehler, *Z. phys. Chem.*, 1916, 91, 705-712; *J.*, 1917, 297.
(12) Tanning Phenomena in Jellies. W. Moeller, *Kolloid Zeit.*, 1916, 19, 205; *J.*, 1917, 465.
(13) Hydratation and Dissolution of Gelatin. M. H. Fischer, *Koll. Zeit.*, 1915, 17, 1-7; *J.*, 1916, 265.
(14) The Adsorption of Chrome Oxide by Hide Powder. A. W. Davison, this JOURNAL, 1917, 258.

American leather chemists have now, in conjunction with the U. S. Tanners' Association, founded a research laboratory of their own. The laboratory is in New York City and the first director is Mr. Jesse Briggs Churchill.

[70] *J. Amer. Chem. Soc.*, 1916, 38, 1982.

Articles of special interest to tanners, in which the relations of the chemist to works are discussed from a practical standpoint are "Chemistry and its Relation to Tanning," by G. T. Laemmle,[71] and "Chemical Control in the Tannery," by T. G. Greaves.[72] It is pointed out, rightly, that in connection with the purchasing of materials alone every tannery could afford its own laboratory. Removing the personal element out of the purchasing also removes a lot of doubt and saves a lot of selling expense. Some firms use high-priced classes of materials in certain processes where cheaper ones would do as well.

Glue Manufacture.

The enormous advance in aeronautics has brought with it an increased demand for the best glues, which are required for joining together the laminae of aeroplane propellers. P. A. Houseman[73] gives an empirical method for testing the quality of the glue used for this work. Pieces of straight grained walnut wood, each 9 inches by 2 inches by ⅜ inch are dried at 36° C. for 24 hours, then roughened by a tooth-plane, and two of the pieces are glued together so that their ends overlap by 2 inches; the area of the glued surface is, therefore, 4 square inches. The glue is prepared by soaking the pieces for about 18 hours in water, then heating the mixture to 60° C. and applying it at this temperature; usually, one part of glue to two parts by weight of water gives a suitable concentration. The joint is clamped under moderate pressure for 48 hours and tested after a further 24 hours, the tests, in duplicate, being made as follows: Regular Test.—The joints are pulled apart in a testing machine, and the breaking strain per square inch of glued surface is recorded. Heat Test.—The joints are heated at 45° C. for two days and then pulled apart, and the breaking strain recorded.

Immersion Test.—The joints are completely immersed in water at 20° C. for 12 hours and then pulled apart. Results of from 450 to over 600 pounds per square inch of glued surface are found in the regular test, and about the same figures in the heat test, while the immersion test results are sometimes lower, and sometimes

[71] This Journal, 1917, 169.

[72] *Ibid.*, 1917, p. 337.

[73] *J. Ind. Eng. Chem.*, 1917, 9, 359; *J.*, 1917, 513.

higher than the regular test results. The addition of a small proportion (5 per cent.) of phenol to the glue solution increases the strength of the joint; addition of ammonia does not affect the regular test results, but raises the heat and immersion test figures. A Swiss casein glue, of the type used on German aircraft, and consisting of about 66 per cent. of casein, 23 per cent. of mineral matter (sodium salts, silica, lime and alumina), and 1 per cent. of petroleum, gave a particularly high result in the immersion test.

F. H. Stevens[74] patents the use of formaldehyde for waterproofing glue joints. The surfaces to be joined are moistened with a solution of formalin (25 per cent. of 40 per cent. formaldehyde) and are then covered with glue in the usual way.

O. Röhm[75] patents the use of pancreatic or similar enzymes which are capable of splitting up or digesting albumin. Instead of the preliminary extended treatment with lime, followed by washing and neutralization with hydrochloric acid, the glue pieces are treated for a few hours with the enzyme solution. After the pieces have been treated in this way they are boiled in the usual manner.

An attempt to ascertain the chemical differences between fish gelatin and bone gelatin has been made by Y. Okuda.[76] Fish gelatin derived from sharkskin was hydrolyzed with hydrochloric acid, baryta, and sulphuric acid, and the products from each investigated. The total nitrogen and its distribution was found to be the same for both sorts; but the fish gelatin gave rather more monoamino acid, and much more glycocoll, alanine, leucine, phenylalanine, glutamic and aspartic acids than the bone gelatin. The proline and serine contents of the fish gelatin formed by the ester method were low, probably the results of experimental errors. The diamino acids were present in about equal quantities in the two gelatins.

In the manufacture of bone glue R. Berliner,[77] Moscow, patents a process in which the bones are treated with sulphur diox-

[74] Eng. Pat. 106,439; *J.*, 1917, 728.
[75] Eng. Pat. 104,181; *J.*, 1917, 1141.
[76] *J. Coll. Agric. Tokyo,* 1916, 5, 355-363; *J.*, 1917.
[77] U. S. Pat. 1,176,644, 1916; *J.*, 1916, 551.

ide; the fat is then extracted, and at the same time the sulphur dioxide is expelled, after which the glue is boiled out.

The chemical analysis and investigation of glues has been neglected in this country, except for the work of Rideal and Trotman. Very useful information on the analysis of glue is given by the latter in his book "Leather Trades Chemistry" (Charles Griffin & Co., Ltd., London, 1908), p. 238, and by the former in "Glue and Glue Testing" (Scott Greenwood & Co., London, 1900), p. 107. Some of the larger glue works employ competent chemists, but very little of their work is published.

LEATHER MAKING IN JAPAN.*

By Lloyd Balderston.

In European and American countries the domestic supply of raw material for leather is comparatively abundant because of the large number of domestic animals slaughtered, whose skins are in general a by-product. In central Japan, one may ride all day on the railway without seeing a domestic animal larger than a chicken, except an occasional dog, and at the more important stations a few draft-horses. It is not surprising, then, to learn that little leather is used by most of the people. Many men in the cities wear shoes, and in wet weather one often sees a man in this land of no sidewalks plodding along a muddy street in high boots which seem to suggest cavalry boots. For outdoor wear the great majority of people use wooden clogs, straw sandals or cloth shoes with rubber soles.

The wooden clog, called "geta," is the correct thing. For muddy weather your geta will be 6 inches high, while in dry weather they are only 2. At the door you step out of the clogs and slip on some sort of slipper in which to enter. The natural gait of a man in clogs is about half that of one in shoes, so people who are obliged to walk rapidly have to use something else. Postmen and the men who pull the quruma (formerly called jinrickisha) have the rubber-soled cloth footgear, and drivers of drays, together with laborers in general, wear a straw sandal tied with straw rope. These cost 2 cents a pair, and you find cast-off samples lying along

* *H. and L.*, Feb. 15, 1919.

the street just anywhere. Much of the harness in use is made of rope or other fiber material.

Under the old regime the little leather used for saddles, harness and certain fittings was made by men belonging to a class of social outcasts called "eta." This fact seems to have added somewhat to the difficulty of establishing modern tanneries in Japan, but so far as I can learn not stigma now attaches to leather workers. There are still many small tanneries about over the country, using for the most part primitive methods. I have seen two such in Sapporo.

The raw material for these small concerns seems to consist mainly of fresh skins of local origin. I saw horsehides, cattle hides, bearskins, foxskins and many dogskins. Most of these were being tanned with alum and salt, some with the hair on and some after unhairing with lime. Alum-tanned cattle hides are made into harness leather by stuffing them with paraffin and grease. Some alum-tanned hides are lightly retanned with oak-bark liquors, and some hides are tanned with oak alone.

Besides the many small establishments scattered over the country, there are now a few large ones with modern equipment. These are nearly all in Tokyo or Osaka or near these cities. On November 1st last year, immediately on my arrival in Japan, I visited the great tannery of the Japan Hide & Leather Co. (Nippon Hikaku Kabushiki Kaisha) in Senju, a suburb north of Tokyo. I had hoped to find here Mr. Miyoshi and Mr. Matsuo, both of whom are members of the A. L. C. A. I had had some correspondence with Mr. Miyoshi in the past four years and anticipated with much pleasure meting him when I should arrive in Tokyo. I was disappointed, however, as Mr. Miyoshi was in Shanghai, and Mr. Matsuo in America. I had not learned that it is the custom of many industrial plants to shut down on the 1st and 15th of each month, just as we do on Sunday. We found the plant mostly idle. therefore, but the chief engineer, Mr. Doikawa, was there, and he was very kind to us, showing my interpreter and myself through the plant. I visited this plant again in August on a working day, and will tell about it when I come to it in order.

At the end of the term in June, I obtained letters of introduction from the university to eight establishments in and near

Osaka, and several in and about Tokyo, hoping to be able to visit them during the summer. I went to Osaka first, late in July, going from Karuizawa, a mountain resort about 90 miles northwest from Tokyo. Starting early in the morning, the day was spent in reaching Nagoya, about 250 miles. The route followed is called the Central Line, being roughly parallel to the coast and midway between the Pacific and the Japan Sea. It traverses a great river valley, devoted to the most intensive rice culture, then, with many tunnels, a stretch of mountainous country, where all available slopes are planted in mulberry for silk culture, and then a wild and picturesque canyon, where for many miles there is no room for the railway in the bottom of the gorge, so that it runs along part way up the hillside, and half the distance through tunnels. The last few miles into Nagoya lie across the flat coast plain.

I spent the night at Nagoya, and from 7 to 1 the next day traversing the 122 miles to Osaka. This also is a beautiful journey, but without the wild features of the other one. Osaka is the most important manufacturing city of the empire, with a population of about one and a half millions, increasing by about 50,000 yearly. It lies on the delta of a river, near the head of the Inland Sea. There are more tanneries about here than in any other part of the country.

Arriving in Osaka, I went in a kuruma to the house of the gentleman to whom I had been recommended to apply as guide and interpreter. He was away, and would not be back till evening. I had learned that Mr. Miyoshi, mentioned above, had been transferred to the Osaka plant of the Japan Hide & Leather Co., so on returning to the station I had them at the information bureau call up the plant. If you will recall the general appearance of a page of Japanese print you will understand why green foreigners ask some one else to call up for them. To my great regret I learned that Mr. Miyoshi was in Tokyo. Then I consulted the head man at the kuruma stand, and showed him the letters I had. He selected four of the addresses, lying in the same quarter of the city, and assigned a man to take me to them.

Osaka lies in the delta of the Yodo River, and is intersected in many places by branches of the river and by canals. There

are a few wide streets, traversed by double lines of trolleys, but most of the thoroughfares are not more than 18 feet wide between building lines. Statistics of the city show that there are something like twenty times as many freight vehicles in the city drawn by men as by draft animals. After riding in a kuruma across the city for nearly six miles, I was quite ready to believe the statistics. The type of man-cart is quite different from any I have seen elsewhere. The puller steers by a tongue, which is removable to save space in parking, and pulls by a rope harness. The loads transported on these carts are incredibly large. Only the uniform level of the streets makes such loads possible, and it is quite evident that in such narrow ways horse-drawn carts could not be used.

For perhaps a mile we followed one of the narrow streets, quite straight, lined with two-story buildings of uniform height, and covered by an awning. The ground floors are all shops, and the street is kept sprinkled and swept so that the whole appearance is very neat and attractive. The awnings are at the roof level, made of light-weight fabric, with metal rings sewed to their edges which run on wires. Each breadth is apparently a yard wide, so that there is plenty of space for air to get through and prevent the awning from being blown to pieces. These awnings represent one of the ways in which the Osaka people strive after comfort in the hot weather. The other is by wearing an incredibly small amount of clothing.

The first plant visited was that of Mr. Nakäi. It is a small plant, privately owned. The proprietor speaks English well, and he very kindly showed me over his plant himself. He makes several kinds of leather, also leather belting. The largest exhibit of finished leather was of black sides for uppers. It was very good leather, and the belts I saw were certainly good looking. The methods here are modern, and the plant is well equipped with machines for one of its size.

Nearby we found the plant of the Nakanishi Company. Here the day was a holiday, so no work was going on, but a young man from the office who speaks a little English took the trouble to show me around. The plant is new, or at least a large part of it must be new. Substantial brick buildings are used for most of the

work. Several kinds of leather are made, but here again most of the finished stock I saw was vegetable-tanned upper, made from light weight hides. Circular vats are used, the vats being in an open yard paved with brick. The materials used here seem to be chiefly oak and wattle barks. The upper stock shown was very attractive in texture and finish. I was informed that some of it was to fill an order from the United States.

My guide took me next to the plant of the Nitta Company, belt makers. They also make sole leather. This company owns a factory in Hokkaido for the manufacture of oak extracts. I had sought permission to visit the extract plant in April, without success, so I was not overwhelmed with surprise at being met here with a firm and prompt refusal when I had presented my letter of introduction, and asked to see the plant. What I saw was a rather imposing brick structure, and an office fitted up in palatial style. Their output includes all styles of leather belts, even link belting, and also balata belting. They also make rawhide pinions.

All this time we were in the far southern part of the city, and another short trip brought us to the plant of the Japan Hide & Leather Co. Here I met Mr. Noguchi, who was in the United States for some time, and speaks the language very well. He apologized for the plant, which is thirty years old. It is doing good work, and compares favorably in appearance and equipment with most tanneries I have seen in our country. The trouble with all these tanneries is that they undertake to make every kind of leather, and to furnish a full line of machines for such a program is an expensive proposition. Here, too, much of the product is upper from cattle hides. Small hides are selected, and shaved to thickness instead of split on the band-knife machine. The bating is done with pigeon dung. Excellent sole leather is also being made at this tannery, which is larger than any other I saw in Osaka. My guide took me back the miles across the city to the Foreign Hotel, which stands on a large island in the river and is perhaps ¾ mile from the station, and charged me the equivalent of about $1.35 for four and a half hours' service, during which he pulled me about 12 miles.

In the evening I called on the gentleman to whom I had been recommended, and he agreed to meet me at the hotel next morn-

ing. On the island near the hotel is a park and children's playground, which was well patronized in the evening. The many boats for hire were all busy, and the whole scene was quite an attractive show. The most striking feature to me was the absence of noise. A Japanese crowd takes its pleasure quietly unless there are a lot of drunken men.

The first plant visited in the morning was in the eastern part of the city, not far from the famous Osaka Castle. At this place no work was going on, because of a holiday, so I found that holidays do not seem to follow any discoverable rule. The proprietor was not very cordial, but showed us some of his products, including belting and well-finished black goat leather. He also showed us his laboratory, which is quite well equipped for a small privately owned plant.

Our next objective was the Osaka Belting Company, and we had a lot of difficulty in finding it. Addresses in Japan are not the accurate things we Americans are used to. In general only the approximate neighborhood is given by the address, and you have to consult some one who knows the region before the place can be located accurately. In this case the policeman we consulted thought he knew, and sent us to a plant which makes steel conveyors. At last we found the place, and learned that the manager was out, and that in his absence no stranger could be allowed to see the plant. We looked at samples of their products, very similar to those of the Nitta Company, drank tea and talked for half an hour. This company claims to be the first to introduce modern tannage methods in Japan. One of the gentlemen told about the early struggles, in which the prejudice of the Japanese against tanning as a degrading occupation had to be fought.

I got a noon train back to Nagoya, where I arrived in the edge of the evening and caught a train for Karuizawa. The best accommodation on this was second class, no sleepers. As the car was crowded, I shall long remember that night of thorough discomfort. The trip taught me a lot about Japan, but not so much as I had hoped about her leather industry.

A few weeks later I went to Tokyo to try to see some of the tanneries in that region. One of the graduates of the University of the Class of 1918 is with Mogi & Co. This firm has its main

office in Yokohama. They do a large business as importers and exporters, handling silk and many other lines of goods. The Tokyo office is in the new Marine Insurance building, a splendid modern structure a stone's throw from the great Tokyo station. One of the lines which the firm is developing is hides and skins, and the young man in question is in the department which handles them.

When I had explained to the manager the object of my visit he detailed the young man in question, Mr. Sato, and another, Mr. Suzuki, a recent graduate of Kyoto University, to accompany me as guides and interpreters. The first step was to the really fine restaurant of the Insurance Building, where we were served with a delicious lunch and I ate my first mango.

We spent the afternoon seeing the Senju plant of the Japan Hide and Leather Company. There we found Mr. Teiji Nagasawa, who had returned a few weeks before from a visit to the United States. He was very cordial and showed us the whole plant, which on this occasion was in operation.

The assortment of hides and skins was very wide, for this tannery, like most that I have seen in Japan, makes many kinds of leather. Wet-salted Japanese and American hides were sorted for size and piled on a cement floor in an airy warehouse. There were great numbers of dry-salted China hides, folded in the familiar manner. We saw many piles of hair-sheepskins from China, also unhaired and pickled goatskins from the same source. From India there were Patna and other goatskins and kips, and finally carabao hides, whose source I did not learn. We saw a lot of these tanned as butts, which we were told were to be used for heavy belting. I think those butts averaged half an inch thick when dry. Beside belt leather, this plant makes sole, harness, heavy upper, chrome goat, and vegetable-tanned goat, also calfskins with the hair for army knapsacks, and I do not know what other kinds.

Heavy leather operations are conducted on wet-salted skins for a week or so, and then shifted to dry-salted for about an equal period. After soaking, the dry-salted hides are softened by drumming for a short time. The liming process offers nothing unfamiliar. Unhairing and fleshing are done by hand. The tannage

for heavy leather involves rockers, suspenders, layaways and retannage or dry-dipping. There is no drumming for the standard product, but I was shown samples which had been made partly in the drum.

The tanning materials used are oak bark, both Japanese and California, wattle bark, quebracho and oak bark extracts and some myrobalans. Both solid and liquid oak bark extracts are used, made at the company's plant at Ikeda, Hokkaido. To produce strong liquors for dry-dipping, a vacuum pan is used, made by the Kestner Company, Philadelphia. The tanned hides are dried in the sun before dry dipping, the dark color thus produced being preferred for sole in the Japanese market. Hides for harness and upper are bated with hen dung. Stuffing is done in drums or by "burning in." Upper leather is made from cattle hides, shaved instead of split with the band-knife machine. The two-bath process is used for chrome goat, which is mostly finished in black. Kid leathers form only a small proportion of the output here, but their quality is quite up to usual standards.

Among the machines for heavy leather which we saw were a setting-out machine of German make, with a movable table, and two types of rolling machine for sole. One of these is a pendulum machine, and the other has its roller attached to a carriage which travels back and forth on ways. A large building is devoted to the making of belting and army knapsacks, with some other smaller items. In inspecting this building we were joined by Mr. Teijiro Kagawa, the company's belting expert, who was with Mr. Nagasawa on his American trip. The belt-making methods are thoroughly modern. The stretching apparatus is quite similar to that used in Philadelphia and Wilmington. The cutting is done by hand instead of machine, but the cut pieces are sorted and placed with the same care used by American makers. The finished belts are quite comparable to standard American brands. On the second floor of the building the knapsacks are made, and here small pieces left from belt making are cut into various small articles.

After we had made the round of the tannery, we came back to the office and were introduced to Mr. Matsuo, mentioned above as a member of the A. L. C. A. He has studied under Eitner and

Kohnstein at Vienna and Procter and Stiasny at Leeds. Certainly the engineers of this company have studied to some purpose. Their plants are using scientific methods and are turning out leather of high quality, which will bear comparison with any I have seen anywhere.

The journey back to the center of the city is a long one, so we had no further time for sight-seeing that day. I went to the Station Hotel, a modern hostelry built and operated in western style, which occupies a large part of the great Tokyo Station building, promising to meet my friends next morning at the opening hour at the office of Mogi & Company.

This plan was carried out, and we were soon on the way to the plant of the Meiji Company, having first telephoned to them and learned that a visit would be welcomed. Their tannery is several miles from the center of the city, to the east, at the head of Tokyo Bay. We went as far as possible by trolley and then in kurumas along canals and between fields of lotus. The lotus was in full bloom, and made a truly gorgeous display. It seemed strange that those splendid blooms, 6 inches across, should be a mere incident in the raising of a food crop. But so it is. The root is what the Japanese are after, though they enjoy the flowers as much as we. The last two blocks were along a canal bank, and as we approached the entrance to the tannery, we saw a barge loaded with the familiar sacks of solid quebracho extract tied up to the wharf. At that temperature it was rather a stretch to call it solid extract, as many streams were visible, coming from holes in the sacks.

I handed in my letter of introduction, and presently the manager, Mr. Seizo Ozawa, came out and greeted us. He told us that he expected shortly to visit the United States, and since I began writing this I have had a card from him from Buffalo and a letter from Mr. Jacobson speaking of his visit to Chicago. Some of the readers of *Hide and Leather* will therefore understand that I did not need an interpreter when Mr. Ozawa took the three of us through the great plant of the Meiji Leather Company. The plant is rather new, and shows the influence of American ideas more than the others I had seen. Mr. Ozawa explained this by telling us that the man chiefly responsible for the plans had studied in America.

Wet-salted hides, American and Japanese, are kept in a concrete cellar, lying in a pile as at the Senju tannery. Dry hides are kept in a room not protected from the heat, and in the warm damp atmosphere they showed some mould. Many of these the company buys in China and has them dry-salted before shipment to Japan. We saw also many Chinese hair sheepskins. The kinds of leather made here include sole, belting, harness, military upper, glove leather from deerskins, sheep linings, etc. Hides for upper stock and deerskins for glove leather are split on a band-knife machine made in Osaka. We saw this machine in operation, and it performs very well. The deerskins are tanned with a preparation of brains, and make a white and very supple leather. Another specialty which we saw was a lot of rabbit skins, partly Japanese and partly Australian, which were being dressed with the fur on to be used for glove backs for the soldiers in Siberia.

The Meiji Company makes belt leather but not belts. They have both types of rolling machine mentioned above, also union splitting machines. Drying lofts similar to those familiar in America are in use for heavy leather, with fan-driven circulation. We saw no leather being dried in the open.

Mr. Ozawa showed us his laboratory, which has all the necessary apparatus and materials for modern tannin analysis, including a rotary shaker and two cans of American standard hide powder. Altogether, the impression we got of the plant and management and the quality of the various products was most favorable.

We got back to the Mogi offices about noon, and again I was the guest of the company at lunch, after which we made a fresh start to find the Tanaka tannery. This time we took an electric train at Tokyo Station, on the belt line which nearly encircles the city. In about 20 minutes we alighted at a station in the southwestern suburbs and took kurumas for a ride of about a mile to the Tanaka tannery. The manager here speaks no English, so I had to depend on second-hand accounts of some things not evident to the eye. We were received with great courtesy, and shown the whole plant. It is privately owned, and is largely occupied in making harness and upper leather for military use. Much of the latter sort is used in the natural tan color, which is very light, the tan-

nage being straight oak bark. The hides are mostly Japanese, and those for upper are split with a band-knife machine. Other machines in use were a Moenus press and a Quirin press made in Osaka. A little work in chrome has been done here, but in the main, for harness, sole and upper the tannage is entirely with oak, except that some myrobalans are used in the sole layers as dusting material. I saw a lot of barrels of oak extracts made by Kullman, Salz & Co., of San Francisco.

The chrome splits are lighter in weight than those tanned with oak, and are mostly blacked for uppers of civilian shoes. Much of the tanning of splits is done in large paddles. All the products which we saw were first class, and the concern certainly deserves the success which it has achieved. We were told that a representative of this firm would shortly visit the United States.

It may be of interest to add to this rather crude sketch of Japanese leather making a few observations on the way leather is used in Japan. There is a large shoe factory in Senju, very near the tannery I have described. I do not know how many other factories there are, but a great deal of the shoemaking is done by hand. The price of hand-made shoes is such as to compete with the factory product. In America when you order a pair of shoes, the shoemaker sends to a shoe-findings house for the uppers, and his work is simply to put the soles on, and then he gets twice as much for the shoes as the same grade factory-made shoes would cost. Here the shoemaker cuts your shoes to order out of the skin which you select, and does the whole thing. I have not worn any Japanese-made shoes yet, but I have seen a number of pairs which would do credit to the best American makers. Most of those worn here, however, cannot look very well after they have been worn awhile, because the almost universal style is the friend of your youth whose American name used to be "Congress gaiter." Perhaps that term has been forgotten too long to convey any impression, so I had better describe the thing. It is simply a shoe whose sides are made of elastic cloth, so that it can be taken off and put on in a second or two. The reason for this style is simply that every Japanese must take off his shoes every time he steps foot in the house, and put them on again when he goes out, and it is a great saving of time and labor to have a kind of shoe

that does not have to be untied. I do not believe it would be possible to make a Congress gaiter so that it would keep its shape very long. The military boots are very good, and as I have mentioned, they are worn by many men not military.

But the most interesting feature of the shoe-making business to me is the ingenious way in which the scraps are utilized. Because shoes are not worn in the house, the soles may be as rough as you please, so hob-nails are much used. Small pieces of sole leather are nailed on to soles in the manner of cleats on football shoes, and these no doubt add a good deal to the life of the sole, as well as furnishing a use for pieces which would otherwise be wasted. Even scraps of upper leather are utilized for soles. A shoe is built of cloth with a felt sole, and then pieces of upper leather are nailed on to the felt with clinched hob-nails, and the heel fortified with an iron piece, and you have a pair of shoes for 60 or 75 cents that are worth the money. I do not believe that very much leather goes into the class of scrap at $5 or $7 a ton in this country.

Worn shoes, whether of leather, rubber or whatnot, are repaired when we Americans would not consider them at all worth it, and this, too, is commendable, where the cost of labor relative to materials is so much less than in our country.

One class of leather product in which Japan holds her own with any country is trveling bags. Suit cases and other bags of the same type but smaller are very much used, and they are splendidly made. The use of leather bags is by no means so general as in America, but the average quality of those seen is higher. If one cannot afford a good leather bag he uses a cloth one, or carries his things in a "furoshiki." That is simply a square of cloth, tied at the corners, and it is amazing how convenient it is when you have got broken to it.

BOOK REVIEW.

ANNUAL REPORTS OF THE SOCIETY OF CHEMICAL INDUSTRY ON THE PROGRESS OF APPLIED CHEMISTRY. Vol. II, 1917. Published by Harrison & Sons, 44-47 St. Martin's Lane, London, W. C. 2. Price to members of the S. C. I., 4/6; to others, 6/6, post free.

A report of the progress of applied chemistry in all branches of the chemical industry, during the year 1917. The different divisions are

treated separately by different editors and include a brief review and a complete bibliography of all important articles and books published during the year. The section on Leather and Glue is edited by Joseph T. Wood, F. I. C., and is given complete elsewhere in this issue. Following is a list of the divisions in the report, with the corresponding editor for each section.

Plant and Machinery. By J. W. Hinchley, F. I. C.
Fuel. By J. S. S. Brame.
Gas. Destructive Distillation. Tar Products. By E. W. Smith, M. Sc., F. I. C.
Mineral Oil. By W. J. A. Butterfield, M. A.
Coloring Matters and Dyes. By Gilbert T. Morgan, D. Sc., F. R. S.
Fibers, Textiles, Cellulose, and Paper. By J. F. Briggs, A. C. G. I.
Bleaching, Dyeing, Printing, and Finishing. By S. H. Higgins, M. Sc.
Acids, Alkalies, Salts, Etc. By H. A. Auden, M. Sc., D. Sc.
Glass, Refractory Materials, Ceramics, and Building Materials. By W. J. Rees, F. I. C.
Metallurgy of Iron and Steel. By C. O. Bannister, F. I. C., A. R. S. M.
Metallurgy of the Non-ferrous Metals. By G. Patchin, A. R. S. M.
Electro-chemistry. By Arthur J. Hale, B. Sc., F. I. C.
Oils, Fats, and Waxes. By E. R. Bolton, F. I. C., and Cecil Revis.
Paints, Pigments, Varnishes, and Resins. By R. S. Morrell, Ph. D., F. I. C.
India Rubber, Etc. By H. P. Stevens, M. A., Ph. D., F. I. C.
Leather and Glue. By Joseph T. Wood, F. I. C.
Sugars, Starches, and Gums. By T. H. P. Heriot.
Fermentation Industries. By Arthur R. Ling.
Water Purification and Sanitation. By S. Rideal, F. I. C.
Fine Chemicals, Medicinal Substances, and Essential Oils. By Frank Lee Pyman, D. Sc., Ph. D.
Photographic Materials and Processes. By B. V. Storr, M. Sc.

ABSTRACTS.

Ionization of Proteins and Antagonistic Salt Action. JACQUES LOEB, *J. Biol. Chem.*, 33, 531 (1918). Into each of three cylindrical funnels were placed 2 grams of finely powdered, non-bleached, Cooper's gelatin, the powder being held in the cylinder by a circular piece of filter paper. Sample No. 1 was perfused six times in succession with 25 cc. of distilled water, No. 2 was perfused twice with 25 cc. of M/8 NaCl and then four times with 25 cc. of distilled water, and No. 3 six times with 25 cc. of M/8 NaCl. In No. 1 and No. 3 moderate swelling occurred, but in No. 2 the swelling was several hundred per cent. greater than in the others.

When the three samples were subsequently dissolved in water to make 3 per cent. gelatin solutions and 5 cc. taken in each case, it was found that No. 1 was precipitated by addition of 5 cc. of 95 per cent. alcohol, No. 3 by 7 cc., but no precipitation occurred with No. 2 however much alcohol was added. When the gelatin from No. 2 is placed in an electric field, it migrates to the anode.

Loeb's explanation of the above results is that gelatin and NaCl react chemically to form a highly ionizable sodium gelatinate. Much swelling was prevented in No. 3 by the excess of salt present; when this is washed away, as in No. 2, the gelatin swells to a greater extent than in pure water.

Numerous experiments were made, all of the above general type, in which the gelatin was treated first with M/8 NaCl and then with various salts of varying concentrations. When the final washings were made with NaCl, it was found that no additional swelling occurred if the concentration of salt was greater than M/64, which Loeb refers to as the *critical value* of the salt. He found a critical value of M/64 for NaCl, LiCl, KCl, NH_4Cl, NaBr, $NaNO_3$, NaCNS, and CH_3COONa. But he found a value of M/128 for sodium sulphate, oxalate, tartrate, and malate, lithium sulphate, potassium sulphate, oxalate, and tartrate, and ammonium oxalate and tartrate. These results indicate that the valency of the anion is without effect, since the critical value always occurs at the same concentration of univalent cation. A change in valency of the cation, however, results in a very marked difference in the critical value. In fact Loeb found that, if powdered gelatin be perfused first with a salt with divalent cation, such as Mg, Ca, Sr, or Ba, and then with distilled water, no additional swelling occurs. The conclusion is that the gelatinates of Mg, Ca, Sr, and Ba are very slightly ionized. This explains the antagonistic actions of a salt with a divalent and one with a monovalent cation. A small amount of NaCl causes swelling of gelatin by forming a highly ionizable sodium gelatinate. The addition of $CaCl_2$ completely counteracts this swelling effect by forming a very slightly ionizable calcium gelatinate.

When gelatin powder is first perfused with M/8 NaCl and then with solutions of glycerol, cane sugar, or ethyl alcohol of concentration less than 2M, the additional swelling, *i. e.*, the swelling in excess of that caused by the salt alone, is practically the same as though distilled water had been used in the final perfusions.

Loeb supposes that excess of salt prevents swelling by repressing the ionization of the gelatin compound. [Abstractor's Note: This supposition is hardly tenable in view of the facts that the gelatin compound is highly ionizable and that any appreciable additional swelling is prevented by concentrations of salt as low as M/64. On the other hand, a completely satisfactory explanation has been given by Procter and Wilson (cf. this JOURNAL, 11, 261 (1916)) who showed that the degree of swelling of gelatin is directly proportional to the excess of concentration of diffusible ions of the jelly phase over that of the external solution, which

value is lowered by adding to the system any electrolyte which does not enter into combination with the gelatin. This explanation has been shown to be in quantitative agreement with experimental determinations (cf. this JOURNAL, 13, 177 (1918).] J. A. W.

The Stoichiometrical Character of the Action of Neutral Salts upon the Swelling of Gelatin. JACQUES LOEB, *J. Biol. Chem.*, 34, 77 (1918); cf. preceding abstract. Loeb refutes the statement that the reactions of colloids do not obey the stoichiometric laws of general chemistry. Experiments of the type noted in the preceding abstract were carried out with HCl and NaOH as well as with neutral salts. Two grams of powdered gelatin were perfused twice with 25 cc. of M/100 HCl and the amount of swelling was noted. This was taken as the height in millimeters to which the gelatin rose in the cylindrical funnels in which the gelatin was placed. The gelatin was then perfused four times with 25 cc. of the salt solution to be tested and the additional swelling noted, the total swelling not being considered. For uni-univalent salts, there was either no additional swelling or a repression of swelling when the concentration was greater than M/64. The additional swelling increased as the concentration decreased, the maximum being obtained with distilled water. For di-univalent salts, such as magnesium nitrate, barium chloride, calcium bromide, etc., the critical value was found to be M/128, or just half of the value for uni-univalent salts, showing that the valency of the cation does not affect the results. But with salts having a divalent anion, as the sulphates, malates, oxalates, tartrates, etc., the critical value occurs at M/512, suggesting that gelatin salts with divalent anions are very slightly ionized.

The experiments were repeated using M/100 NaOH in making the initial perfusions. The results were of the same nature as those described in the preceding abstract for NaCl.

It is concluded that gelatin reacts chemically with HCl forming a highly ionizable gelatine chloride. The addition of a neutral sulphate to gelatin chloride results in the formation of a slightly ionizable gelatin sulphate. Gelatin reacts with NaOH forming a highly ionizable sodium gelatinate. The addition of calcium chloride to sodium gelatinate results in the formation of a slightly ionizable calcium gelatinate. With neutral salts gelatin forms compounds of the nature of that formed with NaOH.

J. A. W.

Temperature Transformation. RALPH C. COOK, *Chemist Analyst*, October, 1918. In few places is the chemist called upon to make more frequent temperature transformations than in the oil laboratory. While most specifications for petroleum products are written in the Fahrenheit scale many are termed in Centigrade and until the latter is more universally used one cannot be too familiar with the relative temperature readings on both scales. The following method has been found most convenient.

To either Fahrenheit or Centigrade reading add 40, multiply by 5/9 or 9/5 as the case may be, then subtract 40.

The advantages of the method are obvious and a rapid mental calculation can be made with little difficulty. In the first place the procedure is always the same—one never has to stop even for a moment to think whether the 32 is added or subtracted or whether before or after the multiplication as in the usual method. Also addition and subtraction of 40 call for a change in only one digit.

From an algebraic standpoint the "why" of the method is at once evident upon the solution of the two equations expressing the relationship between the two scales.

$(F-32)5/9 = C$; and $C = F$ at some point.

Substituting, $(C-32)5/9 = C$ from which $C = F = -40$. That is, at -40 the two scales register the same temperature. Hence, by adding 40 to either reading brings it to a point from which one scale is to the other as 5 is to 9, or as 9 is to 5.

Example :

Convert 230 °F. to °C.

$$\begin{array}{r} 230 \\ 40 \\ \hline \end{array}$$

$$270 \times \frac{5}{9} = 150$$

$$\begin{array}{r} 40 \\ \hline 110\ ^\circ\mathrm{C}. \end{array}$$

Convert 265 °C. to °F.

$$\begin{array}{r} 265 \\ 40 \\ \hline \end{array}$$

$$305 \times \frac{9}{5} = 549$$

$$\begin{array}{r} 40 \\ \hline 509\ ^\circ\mathrm{F}. \end{array}$$

German Shoe and Leather Trade during the War. VICE CONSUL ROBERT L. GRAY, *Commerce Reports.* In 1914 Germany was a very close second to the United States in the shoe and leather trade; together they held practically half of the world's business. Germany, however, was dependent upon foreign markets for a great percentage of the raw stocks used; dependent upon Russia for colt and calfskins; upon India for sheep, kid, and heavy upper leathers, such as kips; and on Argentina for heavy cowhides for sole leather. Thus it is clear that with the exception of a small portion of calfskins the shoe industry of Germany was dependent almost wholly upon imported materials. Horse hides, on account of their inferior quality, were worked up for automobile leathers, welts, harnesses, bags, and military accouterments.

When the war broke out the supply of hides and manufactured leather in Germany was large, and as there were still raw stocks to be imported through the neutral countries, trade in finished leather was not interfered with for some time.

Toward the end of 1914 an organization called the Kriege Leder Aktien Gesellschaft was formed for the purpose of regulating the trade in hides and leather and of preventing profiteering. This organization was under Government supervision, but was capitalized and managed by

tanners and dealers who volunteered their services and their property purely from teelings of patriotism. All profits which exceeded 5 per cent. on the capital invested were to be turned over to the Government.

The Government was won over by the knowledge that the founders were men of good standing and by the surcharge of 30 pfennig (about $0.075) per pound on the raw hides to be paid by the manufacturer or tanner and to be used for augmenting a fund for the future support of war invalids. The raw-hide market was to be capitalized, and the prices were to be fixed for the producer. Later on the prices for the finished leather were to be fixed for the consumer also. The articles of incorporation were drawn up and were approved by the military authorities, and the management was vested in the hands of the patriotic founders. The organization was called for the sake of brevity the Klag, according to the initial letters of its name.

The supplies of raw hides were centralized. The tanner was prohibited by heavy penalties from buying his supplies from anyone except the Klag, and the dealer could sell his stocks on hand only to the Klag. The tanners were notified of the conditions under which they could obtain hides and for this purpose were presented with printed forms which asked for information regarding their methods and capacity, the extent of their present business, the extent of their business for a period previous to the outbreak of the war, etc. Such action was taken on the grounds that the Government must know these things "in order to insure a just distribution of the supplies on hand and to regulate the importation of the articles in question during the war and for as long a time thereafter as should be deemed necessary for the conclusion of trade treaties," etc.

There were numerous drawbacks to the Klag system. The tanner who received the bad allotment had no end of trouble with his customers. The shoe manufacturer had been used to contracting for his supply of leather in advance; and as the leather in the course of manufacture originally intended for this purpose had been taken by the Government and there was no moratorium in Germany, the tanner was compelled to fill a portion of his former contracts with the hides which the Klag was delivering to him. If the tanner got bad hides there were claims from his patrons, litigation, general discontent, and in many cases loss of his old customers altogether.

It was only after most of the stocks were worked up and worn out that the people were able to compel the Klag to lower prices. The first reduction was carried through without direct loss to the tanners, as they were notified that the new scale of prices was not to take effect until after those of hides had been correspondingly lowered.

Later a new maximum price was fixed of still lower prices to go into effect at once. This caused a great deal of dissatisfaction among the tanners, for it meant severe financial loss. It was also the means of a curtailment in the production and consequent shortage of leather, which was felt severely a few months later.

The method of allotment of hides, at first voluntary, was made compulsory. The tanner who wished to get supplies from the Klag was compelled to accept a fixed quantity every month, and to turn over to the Government a stipulated proportion of the leather tanned from the hides at the ruling maximum price. The remainder were for the use of the repairer or shoe manufacturer. It had been customary for the tanner to contract with the shoe manufacturer for the leather at his disposal as soon as he had received his allotment of hides. The fixed maximum price prohibited their sale at a higher figure from the moment the new scale went into effect. The tanner had his vats full of hides which he had bought at high prices, expecting to sell the leather which they would bring for a corresponding amount. As the new ruling went into effect at once, however, he was compelled to deliver at the new price to the Government as well as to the shoe manufacturer. He was willing to do so for the Government, partly because of the profits he had previously made, but not to the shoe manufacturer. There was no maximum price as yet for shoes, so that the manufacturer who had based his prices on the higher maximum for leather and sold his products accordingly had all the advantage. He made a large extra profit at the tanner's expense, from which neither the Government nor the people, however, were receiving any benefit.

As an example of the extent of this measure one tanner made the statement that he would realize some 750,000 marks (normal value of mark, $0.238) less on the sale of the leather in the course of manufacture than he had anticipated making.

This second price reduction brought the margin of profit for the tanner very near to that of peace times, and this, together with the bad quality of the hides available, the condition of the extract and other accessory markets, the difficulty in getting coal and the uncertainty of its delivery, and the delay in getting cars with which to ship the leather after it was tanned, compelled the tanner to take a stand against further peremptory price reductions by the Klag.

Before the outbreak of the war quebracho had practically forced the home-grown tanning materials out of the market. The prices for the small quantities of oak bark which were still used in the old style of tanning were not worth the cost of labor required to gather it. All other extracts and barks, with the exception of a very limited amount of oak and an inferior quality of cellulose extract, were imported. As a result, the war brought extraordinary advances in prices. The supply of quebracho wood was soon exhausted. Solid quebracho extract was still imported for some time and in considerable quantities through the neutral countries, but it commanded high prices and soon disappeared from the market.

Germany was consequently forced to fall back on its natural supplies. Oak bark advanced to 11 marks ($2.62 at normal exchange) and higher for 100 kilos (220 pounds). In 1915 and 1916 a great deal of pine bark was stripped. Oak tree branches up to 8 inches in diameter were also

worked up as far as possible into extracts. The use of cellulose extract increased greatly. The majority of authorities are still of the opinion that it possesses very little real tanning value, but it acts as a filler, which is in demand for a leather tanned only by oak. Inasmuch as the use of all fillers or loaders containing sugar, dextrin, or mineral salts was prohibited, that of cellulose increased. The price for this article has not advanced so much as that of other extracts, being about 30 marks per 100 kilos as against some 16 marks before the war.

The shortage of wooden barrels was felt so severely in the extract business that the whole supply was placed in the hands of one firm in Hamburg, which furnished the barrels at a fixed maximum price. The extract works invoiced them to the tanner at the same price,' and the latter was obliged to return them to the barrel dealer when empty, freight paid, for 3 marks less than he had paid for them. The price to the tanner was 13 marks, and to the dealer 10 marks. The 3 marks margin paid the dealer for repairs and included also his profit.

It is clear that the wearing properties of the leather being tanned were, in consequence of the acceleration of the tanning process required and the absence of so many of the accessories which were considered essential to good tannage in peace times, very inferior.

The shortage of fats, oils, and greases also affected the wearing properties of all kinds of leather. The use of these articles was restricted in the fall of 1915 to a fixed maximum amount per hide. The stocks in Germany were taken over at that time by the Government, with the exception of light mineral oils, and distributed to the tanners in the same proportion as were the hides. Fish oil was practically the only fat oil which could be had in large quantities. The price of this article was fixed at 325 marks ($77.35, normal exchange) per 100 kilos (220 pounds) for common, and 350 marks for medicinal qualities as against prices of 30 and 60 marks, respectively, in peace times. This measure affected only the stocks which were actually in the country at the time. There were no price restrictions placed upon those which were imported later, but the importation by private firms was virtually stopped a short time later through the import monopoly of the Zentral Einkaufs Gesellschaft (Central Purchasing Agency) and the impossibility of being able to send money out of the country without the permission of the Government.

As a consequence, values of all these articles on the open market rose greatly. The ruling prices by the beginning of 1917 for castor oil, fish oil of any kind, neats-foot oil, linseed oil, etc., were 1,500 to 1,900 marks per 100 kilos; for light mineral oils, 120 to 150 marks; for borax 900 marks; for stearin, 200 marks and more; for alum, 1,500 to 1,900 marks; for paraffin, 900 marks; for shellac, 2,200 marks; for carnauba wax, Japan wax, and beeswax, 1,800 to 2,200 marks. At the same time salad oil brought 36 marks per liter. Oil barrels sold for 20 marks apiece. Present prices are still higher.

For a time the tanner was free to sell his lime-house offal to the glue manufacturer at a good profit, but soon the price for this article was

fixed at a low maximum. The glue manufacturers were allowed to work up only a limited quantity for glue, as the greater part after the grease had been extracted went into fertilizers and feed products. The curtailment in the manufacture of glue brought a sharp advance in the value of that article, the market price being 325 marks or more per 100 kilos.

So far only the tanning of sole leather and of heavy vegetable-tanned upper leathers has been referred to. In spite of the fact that the tanning of leathers for other than military purposes and for use in the manufacture of shoes was prohibited, the shortage in light upper leathers became so great that according to reports from Berlin not one-seventh of the demands of the civil population could be met; and the situation will become worse each day until peace is declared. The shortage at present of this material is even greater than that of sole leathers. At the outbreak of the war there were very large stocks of light upper leathers in Germany. The German box-calf tanners were among the largest in the world, and the export trade was very extensive, England being probably the best customer. There were also a number of important chevreau manufacturers and tanners of sheepskins. The war hit this line very hard. The dealers were practically excluded from delivery for war needs. Their products were chrome tanned, and their plants were fitted for chrome tanning only, while the military authorities bought only vegetable-tanned leathers.

There was a certain demand for heavier sortings of box calf for the so-called officers' shoes, but the manufacturing trade was even then so hampered by the shortage of heavy sole leather that even this demand was limited. The manufacturers of light upper leathers were compelled to stand by, their markets gone, their immense stocks on hand, and see the tanners of vegetable leathers working night and day and making money as they had never done before. These conditions lasted until well into 1915 when certain of the manufacturers changed their methods and took up vegetable tanning, but only as a makeshift.

The losses the tanners and leather manufacturers have suffered are irreparable. Their trade is gone, their skilled workmen have been called into service, discharged, and scattered among other trades, and their plants and machinery are idle. And this is the case in every other branch of the formerly great German leather industry, with the exception of the tanners of sole and heavy upper leathers. Even this branch, in spite of the fact that its staffs of experienced workers were to a great extent freed from military service, has lost all the essentials which go to build up quality and world supremacy. It has become simply mechanical. The hides and tanning ingredients available are delivered to the tanners at fixed prices. The method of tannage is specified to them. The finished produce in the condition in which it comes out is taken off their hands at fixed prices. A bookkeeper and a foreman are all the management needed. A knowledge of tanning is hardly considered. When the war is over workmen will have to learn the trade all over again. The war has brought no progress, only retrogradation.

When the tanners of light leathers saw themselves practically shut out from delivery to the Government, they set about to create a market for the stocks of finished goods which they had on hand, and they succeeded so well that by the end of 1915 there was very little light upper leather to be had. Vast quantities were worked up into leather suits and vests and leather-lined clothing of all kinds. The heavier sorts went into leggings, and legging factories sprang up like mushrooms. The stocks of heavy splits were soon got rid of in like manner. The results of this wholesale waste of leather would not have been so disastrous if the Government had reserved for future use a portion of the dog hides then lying in the warehouses, but seemingly no importance was attached to this class of leather. For the winter campaign of 1914-15 practically the entire stocks of sheepskins in Germany and Austria were worked up, with the wool on, into snow coats for the troops in Russia and the Carpathians. To-day the shoe manufacturer has difficulty in getting enough light leather to make the straps and other reinforcements which are necessary to hold the inferior cloth or felt uppers on to the wooden soles of the only kind of shoes which can be made for the civil population.

The trade in traveling bags, women's handbags, pocketbooks, etc., suffered probably more severely than any other branch of the leather trade. They have been given work in making saddles and other military accouterments, but their regular trade was checked by an order issued shortly after the outbreak of the war which prohibited the splitting of leather.

Of the 426 belt factories working in 1914, 400 have been closed arbitrarily.

The shoe manufacturing trade of Germany was formerly the most important in Europe. At the outbreak of the war there were some 1,500 mechanical factories in operation employing some 50,000 skilled workmen. The quality of the output was good, and the export trade was growing rapidly. This branch suffered from the moment the war began, although no particular shortage was felt until toward the end of 1915. The outbreak of the war disorganized the factories by robbing them of their skilled help. Thus the business conditions in the months following made it difficult for the manufacturer to dispose of the stocks on hand at a profit. He had formerly worked to a very large extent on credit, probably more so than had any other large branch, and had sold his shoes to the retailer on still more generous terms. A credit of eight or nine months to the retailer was not uncommon, while the terms of credit to him, with the exception of those with his bank, were from three to six months. When the war broke out, the goods which had been intended for export were left or thrown back upon his hands, and the retailer, in consequence of the easy terms upon which he had been able to buy, was overstocked. The manufacturer's creditors were soon demanding their money and refusing to renew his notes. As there was no moratorium and as the banks were endeavoring to reduce his credits whenever pos-

sible, the manufacturer was compelled, in most cases, to warehouse the stocks on hand or to sell them at a loss in order to meet his creditors.

The shoe manufacturers were not called upon to any great extent to manufacture army boots. As they had not shown themselves willing to meet the military specifications in peace times, the Government had fitted up its own workshops and manufactured its own boots. When the war began, the Government simply enlarged these shops and augmented its staff from the shoe workers who had been called into service.

The period of inactivity for the private manufacturer continued until well into 1915. The only kinds of shoes that were made in any great quantities during this time were the so-called officers' shoes, a heavy, waterproof, box calf variety, which was very well made and which sold for some 30 marks a pair. But the shortage of heavy sole leather hampered the manufacture of this grade of shoes and soon stopped it entirely.

The summer season of 1915 brought a better demand, and the manufacturers protested against the system of the distribution of sole leather by which they were unable to get what they considered sufficient quantities of any kind. Those in charge of the leather stocks, however, saw no need of having additional new stocks until the retailers' supply was considerably reduced.

The retailer naturally raised his prices and continued to do so until a commission was appointed to regulate them and to fix the percentage of profits which the retailer was allowed to make. He was obliged to lay the original invoices for the shoes in stock before the commission and stamp the selling price fixed into the sole of each. It took some months to arrange this, and by that time a shortage was making itself felt. The matter was taken up with the shoe manufacturers' association, and the percentage of profits for all parties was fixed upon. The arrangement allowed for a profit of 35 per cent. between manufacturer's cost and wearer's price. The manufacturer who sold to the wholesaler was allowed 6 per cent., the wholesaler 9 per cent., and the retailer 20 per cent. Where the manufacturer sold direct to the retailer, he was allowed a correspondingly large profit. He fixed and changed his manufacturing cost monthly, according to the market price of the accessories at that time, but he had to keep his factory books so that a control commission would verify his accounts. This measure resulted first of all in a large increase in the price of shoes, an increase which grew from month to month. The manufacturer bought what goods he could and paid the prices asked for them. The higher they were, the better he was satisfied, for 6 per cent. on a pair of shoes which he could prove had cost him 20 marks to manufacture was more acceptable to him than the same profit on a pair which had cost him only 10 marks.

During this time he was able to get a fair amount of sole leather, even if only of the very lightest sorts. But his factory remained so disorganized through the continued drafts upon his workmen, and the great scarcity of laces, thread, and other accessories that it was impossible for him to manufacture in any large way.

The quality of the shoes manufactured was poor. The total absence of rubber cement and all kinds of better qualities of pastes, the inferiority of the linings and thread, the difficulty in obtaining lasting tacks, welting, laces, and their poor quality rendered the manufacture of a good shoe impossible. The upper leather was good, but that was all. The sole leather was of the very lightest weight, a weight which in peace time had been used only for town shoes or women's light boots. The manufacture of shoes with double soles was forbidden.

The wholesaler suffered by the new arrangement. He had conducted his business in normal times more in the way of an agent doing a small business on his own account than in the manner of a wholesaler. He had no large amount of money invested and carried no great stocks, and besides many dubious elements (shoe schiebers), who had become a curse to the trade, made their appearance.

The Government has been endeavoring for some time to inaugurate a system which would give it more control, and in the spring of 1917 an order was issued peremptorily closing 1,100 of the 1,500 factories. An elaborate scheme was worked out in great detail for the continuance of the remaining 400 factories, the main points of which were the following: All Germany was divided into sections and the plants in each section were to consolidate. The shoes thus manufactured were to go into a common stock thence be delivered to the old customers of the individual firms forming the consolidation, according to a ratio based upon the quantities bought by the respective customers during a period previous to the outbreak of the war. As the profits were fixed by law, even the question of their division among previous competitors was relatively simple.

When the scheme was at last worked out, the following conditions prevailed as announced by an official notice from Berlin:

> When we take into consideration the fact that we have a shoe-wearing population of 50,000,000 and that each of these needs one pair of shoes and three pairs of soles a year, we find that our supply of sole leather is insufficient to meet the wants of one-seventh of our population. In addition to this, it must be borne in mind that the quality of the leather on hand is inferior to the quality of leather tanned in peace times. The supply on hand is not sufficient to cover the demands of the miners, the sewermen, and the fishermen, the three classes of workers who must have leather shoes. Our supply of upper leather is still smaller. The manufacture of leather shoes for other than the above-named workmen is prohibited. New shoes for the general public can be made only with cloth uppers and wooden soles.

The one measure which was responsible more than any other for the later shortage or rather total dearth of leather shoes was an order issued in the spring of 1916 taking the sole-leather offal from the Government shops off the open market. Before this order was issued the offal had been sold periodically at auction and, as can be imagined, had brought large quantities of sole leather of good quality into the market. The pieces of the offal were as a general thing not large enough to be used by the manufacturer except for heel building, but they were large enough

to be used by the repairer, and the smallest pieces were worked up by the many firms making sole protectors, so that absolutely none of the leather was wasted. This went to prolong the life of the shoes in wear until a small manufacturer in Berlin conceived the idea of making a universal half sole out of this leather.

The offal was to be sliced into small pieces, which were to be fitted together and the whole held together by flexible wire netting. The Government approved the suggestion and immediately appropriated all offal for the purpose.

The difficulty of getting a plant in working order to make half soles for 50,000,000 people was a problem. The die makers tried to convince the inventor of the impossibility of getting ready the enormous number of dies necessary even to start the business under the existing circumstances. In the summer of 1917, over a year later, a large quantity of the soles was ready, and the distribution began. The first attempts of the repairer to use them, however, proved their impracticability.

Not only has the war exhausted the supply of shoes, but it has ruined the business for years to come. The tanner may be able to take up his trade in the old way after he is once able to obtain the materials needed; but one cannot manufacture shoes with unskilled labor, and even the most skilled worker losses his efficiency when he is taken away from his regular work for a time. So, it will be years, even with the help of the remnants of the 50,000 skilled workmen who may return from the war, before a new staff of efficient help for the manufacture of shoes can be again built up.

With the falling away of the great demands made by the German armies upon the supply of leather, the prospects of satisfying the civil population have naturally somewhat improved. The soldiers, upon their discharge from the army, will be supplied with shoes from the military stock on hand. It is not known how large this supply is or whether it is possible to distribute from it shoes to the civil population, but it may be safely assumed that the reserves will not be sufficient to meet even the needs of the soldiers. It will be necessary to reduce further the amount of leather allotted to the factories 20 to 25 per cent., which amount has already fallen to about 50 per cent. of the remaining stock on hand before the war.

An appreciable amount of upper leathers used in the manufacture of gas masks can be supplied from the stocks held by the military authorities owing to the fact that the manufacture of gas masks has been discontinued.

It is now the hope that a great many animals used for military purposes will be brought back with the armies and that the stock of hide-producing animals fit for slaughter will thereby be greatly increased; but even these animals are by no means able to replace the great loss occasioned by the evacuation of the territories occupied by the Germans in the east and the west since the first year of the war. Furthermore, a great number of the most important tanneries and leather and shoe

factories are located in the Provinces of Alsace and Lorraine (Strassburg, St. Julien, St. Ingbert, etc.). The Germans, realizing that the loss of these factories will deal a severe blow to the shoe industry, are bending every effort to the end that the traffic in this connection between the right and the left Rhine territory remain unmolested with respect to German interests. The belief, however, that in a brief time the shoe shortage will be entirely removed is premature.

The Egyptian Hide and Skin Market. CONSUL ARTHUR GARRELS, *Commerce Reports.* Hides and skins emanating from Egypt fall into the following classes: Egyptian woolen sheepskins, lambskins, goatskins, buffalo calfskins, oxhides, buffalo hides, and camel hides.

Egyptian woolen sheepskins come from Upper Egypt and are divided into two categories, Saidi and Behera. The season for the Saidi skins begins in February and ends in April. The quality is inferior. They are usually cased and salted. The output approximates 125,000 to 150,000 pieces annually. These skins are mostly purchased by native traders, who remove the wool and dispose of the skins to local tanneries where they are made up into basils (a trade name signifying a bark-tanned thin leather). The Saidi sheep is of black color. It is never shorn. The weight averages between 7 and 8 pounds per salted skin. The season for the Behera skins begins in May and lasts until about the middle of December. The annual production of Behera skins is about 200,000 pieces; they are cased and salted. About 10 per cent. are black and 90 per cent. white and fawn. The skins are sold in lots by weight without classification or distinction as to whether the skins are shorn or not. The average weight per skin is about 5 to 6 pounds per piece. About 50 per cent. of the annual production comes on the market as all-wool skins; these average 10 pounds per skin; 25 per cent. are half wool and 25 per cent. shorn, averaging 5 pounds and 3 pounds, respectively, per skin. The Behera skins are used mostly by the local tanners for the production of basils. Basils are chiefly exported, the largest part going to the London market.

Lambskins likewise come from Upper Egypt and are also of two classes: Saidi and Behera. The season for lambskins begins in May and ends in August. The Saidi lambskins are black, while the lambskins from Behera are generally white; a small proportion, about 10 per cent., being black. They are generally cased and salted, but may also be obtained sun-dried. The annual output of Egyptian lambskins approximates 100,000 pieces, of which 70,000 are Saidi skins. Saidi skins will average 165 to 175 pounds per 100 skins; Behera skins 155 to 165 pounds. Before the war Egyptian lambskins were largely exported to Austria via Trieste. Prices of sun-dried skins are from 4 to 6 cents per piece higher than salted skins. Sun-dried lambskins are usually sold per piece. There is very little difference either in price or quality between the Saidi and the Behera skins.

Upper Egypt too produces the larger amount of goatskins, the annual output of which is approximately from 450,000 to 500,000 pieces, usually cased and dry-salted. The season for goatskins begins in April and ends in early December. Occasionally random lots come upon the market later. Such out of season appearances are the result of hoarding for higher prices by native sellers. Goatskins average 185 to 187 pounds per 100 skins.

Buffalo calfskins are likewise an Upper Egypt product, and like sheepskins are classified as Saidi and Behera. The buffalo calfskin season begins in August and lasts to March. About 250,000 pieces make up the yearly output, which is divided equally between Saidi and Behera. They come upon the market either dry or salted. Dry Saidi buffalo calfskins average 3½ to 4 pounds per piece; Behera, 6 to 6½ pounds; salted Saidi, 2½ to 3 pounds; Behera, 3½ to 4½ pounds. A difference in price between the two qualities varying from 30 to 33 per cent. usually pertains. Buffalo calfskins are always in great demand. Purchase terms usually embrace a 5 per cent. allowance for seconds. But the actual amount is 15 to 20 per cent. The term "seconds" embraces such skins as are holed and have become almost useless through deterioration. Skins 50 per cent. deteriorated and 50 per cent. in good condition are considered firsts. These skins may be had both sun-dried and salted. Large quantities are produced at the Cairo and Alexandria slaughter houses. Slaughter house skins usually bring a higher price than those coming from country-killed animals. Cairo and Alexandria produce about 1,000 buffalo calfskins per month, the larger part of which are exported. Buffalo calfskins from the provinces are consumed by local tanneries. A portion, however, still remains for the export trade.

Throughout Egypt large numbers of oxen and calves are slaughtered daily. Hides coming from the abattoirs of Cairo and Alexandria are of superior quality to those emanating from the country at large. The abattoir hides, including those from Assuan, are better finished than the others. For market purposes hides are divided into two classes, slaughter house hides and hides emanating from the provinces. Before the war a large proportion of Russian and Syrian cattle were slaughtered at Alexandria and Port Said. The hides emanating from other districts come entirely from Egyptian-bred cattle. Cattle quarantine regulations prohibits the introduction into the interior of cattle of foreign origin. All imported cattle, therefore, must be slaughtered at the port of arrival. Hides are prepared, sun dried, and salted. Skinning in the country districts is far from carefully done. The proportion of holed hides, therefore, is very high. In consequence hides, as is the case with buffalo calfskins, are classified as firsts and seconds. Dry hides vary in weight between 9 and 15½ pounds per piece, the average being about 13 pounds. Hides under 9 pounds in weight are considered as calfskins. The price of slaughter house hides is from 20 to 25 per cent. higher than that for hides coming from provincial districts. The season for hides is perennial, and the business of marketing hides largely distributed. In spite of the careless

preparation and handling to which hides in Egypt are subjected there appears to be no lack in their demand. At present prices for hides make business almost prohibitive.

The conditions and circumstances governing ox hides likewise pertain to buffalo hides. Buffalo hides are exceedingly heavy. The majority of the product is consumed by local tanneries for the manufacture of sole leather.

Camels are perennially slaughtered in Egypt. The annual output approximates 100,000 pieces equally divided between male and female hides. This figure does not include hides from small camels. European and American markets appear not to be interested in camel hides. The major portion of camel hides coming upon the Egyptian market are consumed by local tanners. During pre-war times a small export of camel hides prevailed from Egypt to the Greek Islands. Average weights of salted camel hides are: Male 45 to 55 pounds; female, 33 to 44 pounds. Camel hides are sold per piece. Small camel hides are sold in comparison with their size to large hides, two or three small hides having the value of one larger hide.

No inconsiderate quantity of hides and skins emanates from the Anglo-Egyptian Sudan. Exports from the Sundan for 1916 are given as 750 tons of hides and 362,000 pieces of sheepskins and goatskins.

Sudan hair-sheepskins come from all parts of the Sudan. The better grades are generally dry-salted. Inferior grades as a rule are not salted. The season for these skins runs from September till March. About 20,000 pieces are produced by the Cairo slaughter house. Skins coming from the Sudan are shipped during all months of the year and are generally cased without head. Average weights are 3 to 3½ pounds. Some, however, run as low as 2 pounds per piece. A limited quantity of 4-pound skins also comes upon the market. Skins emanating from the Red Sea and the Kassala Provinces are in great demand, especially in England and the United States. They are generally shipped mixed, but may be obtained sorted if desired.

The same particulars which apply to Sudan hair-sheepskins attach to Sudan goatskins. Sudan goatskins have an average weight of about 1 to 1¼ pounds. They are generally salted, but also may be obtained sun-dried. Recently there has been a great demand for goatskins and prices have risen considerably.

In the Egyptian trade Sudan hides are classified as air-dried and dry-salted. A certain quantity of so-called Sudan hides comes from Abyssinia. Air-dried hides weigh from 10½ to 14 pounds and salted from 12 to 16½ pounds. Occasionally it is possible to make up lots of air-dried Sudan hides of 9-pound sizes. A very small quantity of 6-pound hides is also in evidence. Salted hides sometimes exceed 18 pounds in weight. Those coming from Khartum Province often reach 27 to 30 pounds, although for the most part they do not average more than 20 pounds. Hides from Kassala, Berber, and Red Sea Provinces are less salted than others. Sudan hides are packed in mixed assortments of

firsts, seconds, and thirds. Thirds make up a very small proportion of the package.

Arabian skins coming into the world markets through Egypt and the Sudan originate exclusively in Jedda and places in the vicinity of Mecca. They embrace cattle hides, sheepskins, goatskins, and camel hides and are generally dry-salted. Arabian hides are limited in quantity; the quality, however, is excellent and the pieces well preserved. Sheepskins come from Arabia in large quantities. They are woolen and cased. Such sheepskins average 3 to 3½ pounds. Arabian goatskins are similar to those of the Sudan and weigh from 1¾ to 2 pounds. Camel hides from Arabia are salted and skinned in three pieces, two of which represent the body of the animal and the third the neck without the head. Arabian camel hides are available in greater quantities than ox hides. Merchants insist upon selling ox hides and camel hides mixed together. It is not possible to obtain ox hides without also purchasing camel hides, and *vice versa.* The weight of a whole camel hide varies from 26 to 30 pounds. There is no exportation from Jedda at present, but restrictions probably will be removed in the near future.

The Preservation of Plant Juices for Analysis of Sugar Content. D. O. SPRIESTERSBACH, *J. A. C. S.*, 40, p. 431. There are times when it is desirable to preserve samples for future analysis. Certain fruit juices which are to be tested for their sugar content are subject to change on standing due both to the destruction of sugar by fermentation and change by hydrolysis. (This is also true of many solutions in tannery chemistry, especially the water extraction from leather.—Abst.) Of the many preservatives tested by the author the only ones that were satisfactory were mercuric iodide dissolved in potassium iodide solution, phenol, and toluene. Of these the mercuric potassium iodide and the toluene are the best, particularly in boiled samples which have been made slightly alkaline. The recommended procedure is to take a sample of definite volume, neutralize with a slight excess of calcium carbonate, boil for a few minutes, add 2 grams of anhydrous sodium carbonate per liter of solution, then add the preservative, cool to the original temperature, make up to the original volume, and shake well. The toluene added should be sufficient to saturate the solution and leave a little on the surface (about 5 cc. per liter will do ordinarily). The mercuric potassium iodide should be about 0.1 per cent. on the weight of the solution. Several tables are given showing the effects of the preservatives on solutions after long standing. Mercuric nitrate was used and the preliminary trials indicate that it may be the most effective preservative tried. W. A. F.

Journal of the

American Leather Chemists Association

Vol. XIV | MAY, 1919 | No. 5

W. K. ALSOP . . . . Editor and Manager
G. W. SCHULTZ . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $6.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized July 16, 1918.

ELECTIONS.

ACTIVE.

Ralph Hart, 286 Summer Ave., Newark, N. J.

ASSOCIATE.

Charles Ira Forner, 243 Queens Ave., London, Ontario, Canada.
Charles L. Robinson, % Elkins Tannery, Elkins, W. Va.
S. Sawayama, % Gochakuya, Itokuji Machi, Himeji Shi, Japan.
Leigh Irving Holdredge, % Wallace & Tiernan Co., Inc., 349 Broadway, New York, N. Y.

OBITUARY.

WILLIAM ALLEN FOX.

William Allen Fox died March 26th from pneumonia after an illness of about one week. He had been Associate Editor for the past eighteen months and the Association has been largely indebted to him for conducting the JOURNAL during that unsettled and rather trying period. He was a member of the Council of the Association from December, 1914, to June, 1916.

Mr. Fox graduated from Pennsylvania State College in 1904 and during that year was employed in the laboratory of the Central Leather Company in New York as a chemist. He came with the writer from there to Ridgway in 1908. From 1912-1916 he conducted a laboratory at N. R. Allen's Sons Co., Kenosha, Wis., returning from there to Ridgway, and at the time of his death was first assistant chemist here.

In 1915 he married Miss Josephine Thomas of Kenosha, Wis., who, with a young son, survives him.

The writer, who was intimately associated with Mr. Fox for fifteen years, desires to express a sense of his and the Association's loss in his untimely death in his 37th year.

W. K. ALSOP.

CHANGE OF PROFESSORSHIP IN THE LEATHER INDUSTRIES DEPARTMENT AT LEEDS UNIVERSITY.

Douglas McCandlish, M. Sc., has been appointed to the chair of the Leather Department at Leeds University, England, succeeding Professor Procter who again retires from this position after having reassumed it at the request of the University at the beginning of the war.

Douglas McCandlish was born in Leeds, England, of Scotch parents. He graduated from the University of Leeds in 1905, taking the degree of B. Sc. in chemistry, after which he became an assistant to Professor Procter in the leather department of the university. During his stay at the university he devoted part of his time to work in the laboratory of the city analyst. In June, 1907, he became chief chemist for A. F. Gallun & Sons Co., of Milwaukee. In November, 1908, he returned to Leeds as chemist for William Paul, tanners, but in May, 1910, returned

to his former position with A. F. Gallun & Sons Co. In 1915 the University of Leeds conferred upon him the degree of M. Sc. in recognition of his work since leaving the university.

Professor Procter continues as the director of the Procter International Research Laboratory which is also connected with the university.

SIXTEENTH ANNUAL MEETING.

The following program, subject to some slight changes, has been prepared for the Sixteenth Annual Meeting at Atlantic City, N. J., May 22, 23 and 24:

Morning Sessions Convening at 10 o'clock.
Afternoon Sessions Convening at 2 o'clock.

THURSDAY MORNING, MAY 22, 1919.

Opening Remarks by the President........................R. W. Griffith
Report of Secretary-Treasurer..............................H. C. Reed
Committee Report..J. B. Churchill
(Sulphuric Acid in Leather)
Committee Report...L. E. Stacy
(Preparation of Leather Samples for Analysis)
Committee Report..J. A. Wilson
(Extraction of Grease and Oil from Leather)
Notes on the Determination of Water Solubles in Leather
R. W. Frey and I. D. Clarke
Address ....F. P. Veitch

THURSDAY AFTERNOON, MAY 22, 1919.

Tannery By-Products................................ Van A. Wallin
The Application of Colloid Chemistry to the Leather Industry
John Arthur Wilson
Dyestuffs on Leather..............................Dr. John C. Hebden
Natural American Dyes............................Charles R. Delaney
Dyeing of Leather..C. Propach
Waterproofing Leather..................F. P. Veitch and H. P. Holman

FRIDAY MORNING, MAY 23, 1919.

Committee Report..J. M. Seltzer
(Determination of Total, Soluble and Insoluble Ash in Leather)
Committee Report.......................................C. M. Kernahan
(Sulphite-Cellulose in Synthetic Tans, Tanning Extracts and in Leathers)
Committee Report......................................John H. Yocum
(Practical Uses for Niter Cake)

The Tanning of Shark Skins..........................Dr. Allen Rogers
The Chemistry of Chrome Tanning...................Mabel E. Baldwin
Method for Testing Materials for Increasing the Water Resistance
of Sole Leather.....................H. P. Holman and F. P. Veitch
Address (The Chemist and the Industry)................Fred A. Vogel

FRIDAY AFTERNOON, MAY 23, 1919.

Waste Pulp Mill Bark as a Source of Tannin........Vance P. Edwardes
Sulphonated Oils....................................Dr. C. G. Bumcke
War Activities of the Forest Products Laboratory, Illustrated with
Motion Pictures...............................Vance P. Edwardes

SATURDAY MORNING, MAY 24, 1919.

Committee Report.......................................G. W. Schultz
(Sulphonated Oil Analysis with Particular Reference to the
Hart Modifications)
Committee Report..R. W. Frey
(Kaolin for Tannin Analysis)
Committee Report..T. A. Faust
(Effect of Hard Water on Tannin)
Note on the Relative Absorption of Oils and Greases by Wet and
Dry Leather........................H. P. Holman and F. P. Veitch
The Solvent Action of Petroleum Ether, Sulphuric Ether and Chloroform on Leather Stuffing Oils and Greases
F. P. Veitch and M. G. Hunt

Executive Session.
Election of Officers.
Council Meeting.

PROPOSED CHANGES IN METHODS.

The following proposed changes in the methods of the Association have been received from the Secretary for publication:

PROPOSAL TO ADD TO THE PROVISIONAL METHODS OF THE A. L. C. A. A METHOD FOR DETERMINING OILS, FATS AND WAXES IN CHROME-TANNED LEATHER AND IN COMBINATION TANNED LEATHER.

Extract 5 to 10 grams of air-dry leather in a Soxhlet apparatus until free from grease, using freshly redistilled chloroform as solvent. Evaporate solvent and heat in oven at 100° C. for 30 minutes. Desiccate for 15 minutes at room temperature and weigh. Heat again for 30 minutes, desiccate, and weigh. Repeat until the extract does not lose more than 5 milligrams in weight upon 30 minutes heating.

Signed: JOHN ARTHUR WILSON,
Chairman of Committee for Extraction of Grease and Oil from Leather.

PROPOSAL TO CHANGE THE OFFICIAL METHOD OF THE A. L. C. A. FOR DETERMINATION OF OILS, FATS AND WAXES IN VEGETABLE-TANNED LEATHER.

Change the first paragraph of Section (3) to read:

"Extract 5 to 10 grams of air-dry leather in a Soxhlet apparatus until free from grease, using freshly redistilled chloroform as solvent. Evaporate solvent and heat in oven at 100° C. for 30 minutes. Desiccate for 15 minutes at room temperature and weigh. Heat again for 30 minutes, desiccate, and weigh. Repeat until the extract does not lose more than 5 milligrams in weight upon 30 minutes heating."

Signed: JOHN ARTHUR WILSON,
Chairman of Committee for Extraction of Grease and Oil from Leather.

PROPOSAL TO CHANGE THE PROVISIONAL METHODS OF THE A. L. C. A. FOR THE ANALYSIS OF ONE-BATH CHROME LIQUORS.

Change the name "Acid Determination" to "Available Acid."

Replace the determination of "Basicity" by the following determination of "Relative Available Acidity" which may be called "Acidity" for short:

"Divide the number of gram equivalents of available acid per unit of sample by the sum of the numbers of gram equivalents of Cr_2O_3, Al_2O_3, and Fe_2O_3 per unit of sample, carrying the quotient to two decimal places. As examples, the acidities of the following compounds are given: $Cr_2(SO_4)_3$, 1.00; $Cr_2(OH)Cl_5$, 0.83; $FeOHCl_2$, 0.67; $Cr_2Cl_3(OH)_3$, 0.50; $Al(OH)_2Cl$, 0.33; $Cr_2(OH)_5Cl$, 0.17; $Cr(OH)_3$, zero."

Signed: JOHN ARTHUR WILSON.

LEATHER ANALYSIS.

In the Committee Report on Extraction of Oil and Fat from Leather by John Arthur Wilson, Chairman, is a reference to the need of concerted effort to improve our methods for leather analysis in general. These remarks are timely and it is our purpose to comment somewhat upon these methods. In the first place we have an official method for the analysis of vegetable-tanned and nothing in reference to mineral-tanned leather except a provisional method for the determination of chrome in chrome-tanned leather.

In some instances the methods for the analysis of vegetable-tanned leather have not been worked out with the care exercised in getting together our methods for the analysis of tanning materials. It is doubtful if any of the methods for the different

determinations are generally satisfactory as given, with the possible exception of that for nitrogen. It seems to us as though some of them might be and some must be improved. We are pleased that committees are at work this year on several subjects and hope that this is the beginning afresh of a concerted attempt to materially improve them.

1. *Preparation of Sample.*—This is very satisfactory as far as it goes, but it does not go very far. It is entirely possible to prepare quite satisfactory samples of certain kinds of leather and the method should specify the preparation or at least how it may be done and we hope this will be the outcome of the committee work this year.

2. *Moisture.*—It is doubtful whether drying at 95°-100° C. for 16 hours is as accurate in all cases as a much shorter time at a temperature slightly in excess of 100° C.

3. *Fats.*—Apparently hydrocarbon oils and paraffine wax are fats! The committee work this year has demonstrated that petroleum ether does not extract all the added oils and fats from leather when certain classes of materials are used. Whether the work has advanced far enough to warrant the substitution of chloroform for petrol in all cases is still quite a debatable question.

4. *Ash.*—This matter is in the hands of a committee and the report is elsewhere in this number.

5. *Water Soluble Material.*—In our opinion a certain type of extractor should be specified in which the leather and extract come only in contact with glass and details of the method for extraction should be given. Should the leather be extracted at 50° or at 25°? We have often heard of people getting into hot water, but not of making a practice of walking in it. It might be well to consider the method lately put out by the S. L. T. C. We believe, in view of the use of the extract later for the determination of sugars, that it would be better to have a more concentrated solution. There is nothing to be gained, and possibly sometimes something lost, by soaking a finely divided sample over night before extraction. As to the need of improvement in method, members are referred to the report of the Ash Committee and Mr. Wilson's report in the April number.

6. *Glucose.*—This method certainly needs some work done on it. Together with Mr. J. B. Churchill, we have done some experimenting, but so far have not found out to our satisfaction the reasons for some of the erratic results obtained. We have demonstrated that sodium carbonate should not be used for neutralizing the solution after inversion. In our laboratory work we have used sodium hydroxide and observed with some leathers considerably higher results when carbonate was used. This was especially noticeable if the leather contained magnesium salts and is due to the fact that the hydroxide precipitates the magnesium from the solution and the carbonate does not. In the latter case the magnesium is later thrown down by the strongly alkaline Fehling's solution and is weighed as cuprous oxide. There may be a difference of opinion as to the use of magnesium sulphate, but surely no one wishes to make it do double work in this manner.

As intimated above we believe that more concentrated solutions would give better results. We hope to publish a paper in collaboration with Mr. Churchill which may be of assistance in respect to this particular part of leather analysis.

7. *Nitrogen.*—We have always used 1.5 grams of leather, believing that a more representative sample is obtained than with 0.7 gram, the divisor doubled and are not aware of any more error in the determination.

The question of sampling is a very important matter and something should be done in reference to it. If it does not seem practical to lay down hard and fast rules to apply in all cases, it should be possible to supply information of material value to assist in getting more representative and uniform samples and prevent some of the misinformation due to improper sampling.

W. K. Alsop.

NOTE ON THE EFFECT OF LONG SOAKING ON THE COMPOSITION OF SOLE LEATHER.

By J. B. Churchill.

Some months ago Mr. George H. Raymond, of Hans Rees Sons, Inc., called my attention to a sample of sole leather sent to him by J. T. Wing & Company of Detroit. This sample was taken from a considerable quantity of leather which had formed

a portion of the cargo of the steamer "Pewabic" sunk in Lake Huron in 1865 and had remained under water until October, 1918. Mr. Wing reports that when taken from the steamer the wet leather was pliable and dark red in color, but when dried out became nearly black and very brittle.

The sample received from Mr. Raymond was a square 8 by 8 inches, very dark red in color and almost black on the grain side, but somewhat lighter on the flesh. Inside it showed a deep mahogany color. Its thickness was about 12 iron.

Thinking that it might be of interest to ascertain the effect of this long soaking on the composition of this leather the following analysis was made:

	I.	II.	Average Per cent.
Moisture	10.61	10.60	10.61
Ash	1.27	1.28	1.27
Insoluble ash	1.26	1.26	1.26
Oil and grease	0.34	0.32	0.33
Water soluble	1.78	1.80	1.79
Tans	0.08	0.08	0.08
Non-tans	1.71	1.72	1.71
Hide substance	74.2	74.4	74.3
Glucose and salts	Absent		

On Absolutely Dry Leather.

Hide substance	83.12
Load	16.88
Combined tannin	13.11

The above figures show an extremely high hide substance value calculated on the basis of dry leather and an extremely low value for combined tannin.

It is regrettable that it is not possible to compare these results with figures showing the composition of the original leather. It would seem to us that they point to the fact that long soaking even in water at the ordinary temperature may very slowly remove the greater portion of the combined tannin.

It was with the thought that these results might be of possible interest to others that they are sent in for publication.

AMERICAN LEATHER RESEARCH LABORATORY,
80 South St., New York.

March 14, 1919.

THE RESURRECTION OF UNCHROMED HIDE POWDER.

By Roy H. Wisdom and William A. Felder.

The question has been raised in this laboratory as to the legality of using chromed hide powder, notwithstanding its many advantages. The reason advanced was that in the textile industry, chrome in certain forms is used as a mordant and the supposition was that chromed hide powder acting in this capacity would take up coloring matter which unchromed hide would not absorb. In addition, the analogy between chromed hide powder and chrome tanned leather was sufficient to awaken suspicion, for we all know the affinity chrome tanned leather has for the natural dyestuffs.

It occurred also to us that in the dim past, when the A. L. C. A. was in its infancy and the subject of chromed hide powder was actively discussed, especially at the annual meetings, there used to be a goal toward which every ambitious leather trade chemist cast his eye. It was the production of a dry chromed powder which could be added direct to the tan solution without any preliminary wetting out or washing. The advantages were so obvious that almost every member of the Association at that time had his little fling at it, but the present day still finds us using the same old wet chromed powder.

Another reason was the nearer approach of the laboratory to the tannery, regardless of the fact as to whether the results were in terms of tannin or "matters absorbable by hide." The method is at best empirical.

The above reasons are all given to justify the experiments which follow and, while the writers feel that the stone falls far short of killing all three birds, a sufficient amount of information has been gained to make it of interest to the Association.

The experimental method has for its basis, the direct use of the dry unchromed hide powder just as it comes from the manufacturer. It is added direct to the tan solution without wetting out or washing and is of the grade known as American Standard, probably used in every leather trade laboratory in the United States. Certain adjustments as to amount of hide powder, time of shaking, and condition of tannin solution were made and after many experiments, the following method was fixed upon.

Acidify 200 cc. tannin solution of official strength, with 50 milligrams oxalic acid (dry). Then add 12 grams air-dry hide powder (15 grams for sulphite-cellulose extract), shake for 20 minutes and proceed as in official method. The calculation is made direct, no dilution factor being used despite the fact that the air-dry powder contains approximately 12½ per cent. water.

It will be noted that the above method calls for an added amount of acid. It was found that, under these conditions, the present acidity of the powder was insufficient, as soluble hide appeared in many cases where the addition of acid removed this condition.

It was also found necessary to use a larger amount of hide powder when working with sulphite-cellulose extracts, in order to pass the gelatine-salt test. We would state here in passing, that the non-tannin solutions of all sulphite-cellulose extracts tested in this laboratory, using the official method, failed to pass the gelatine-salt test.

This method also requires an increase in the time of shaking.

The results which follow also include tests using unchromed hide powder, wet out and washed as in the official method.

TABLE I.—NON-TANNINS.

Material	Chromed powder Official method	Unchromed powder Dry method	Unchromed powder washed
Tannic acid	7.23	10.42	7.00
Chestnut extract	15.41	15.89	15.52
Chestnut extract	12.56	12.79	——
Chestnut extract	16.99	16.94	——
Oak bark extract	20.24	19.25	21.00
Oak bark extract	15.04	14.59	——
Hemlock extract	14.92	13.25	15.33
Hemlock extract	14.64	14.01	15.06
Hemlock extract	15.29	14.90	——
Quebracho extract, clarified	5.90	6.03	——
Quebracho extract, clarified	6.36	6.36	——
Quebracho extract, clarified	6.67	6.74	——
Quebracho extract, ordinary	7.12	8.18	——
Quebracho extract, ordinary	7.02	7.84	——
Sumac extract	21.13	21.17	21.15
Sumac extract	18.98	19.29	——
Divi-divi extract	15.20	14.93	15.74
Sulphite-cellulose extract	29.29A	27.11	28.00
Sulphite-cellulose extract	29.78A	27.11	——

A—Positive test for tannin.

In working out this method, the aim at all times was to secure non-tannin solutions which would pass both gelatine-salt and soluble hide tests. The results in all cases practically attained this perfection, but the fly in the ointment appeared when testing for chlorides. Unfortunately or otherwise, a blank test on our American Standard hide powder, according to the experimental method shows a reading of 11.8 milligrams chlorides as NaCl, per 100 cc. solution. In view of some of the non-tannin results obtained, it is questionable whether anything of practical value would be gained by removing the chlorides from the powder or by using a correction factor, providing, of course, that the chromed powder results are reasonably correct. In connection with this a blank was run on the chromed powder according to the official method and resulted in a total solids reading of 4.5 milligrams per 100 cc. solution, presumably sulphates and some chlorides. Further qualitative testing of the non-tannin solutions for sulphates and chlorides led to the conclusion that possibly there was an action between the tannin solution and the sulphates and chlorides in the powder. Accordingly, quantitative tests were made on various non-tannin solutions with the following results.

TABLE II.—CHLORIDES.

All results in milligrams NaCl per 100 cc. solution.

	Non-tannins from dry unchromed hide	Non-tannins from chromed hide Official method	Difference
Tannic acid	12.8	1.7	11.1
Chestnut extract	20.4	1.7	18.7
Oak bark extract	20.4	2.3	18.1
Hemlock extract	19.9	2.9	17.0
Quebracho extract	24.6	2.9	21.7
Sulphite-cellulose extract	38.0	3.5	34.5

TABLE III.—SULPHATES.

All results in milligrams SO_4 per 100 cc. solution.

	Non-tannins from dry unchromed hide	Non-tannins from chromed hide Official method	Difference
Tannic acid	0.7	1.5	0.8
Chestnut extract	1.6	11.6	10.0
Oak bark extract	2.0	6.8	4.8
Hemlock extract	1.2	14.9	13.7
Quebracho extract	6.6	17.8	11.2
Sulphite-cellulose extract	18.7	44.7	26.0

From the above tables, it is quite evident that an action takes place during the shaking process which results in the appearance in the non-tannin solutions of increased amounts of both chlorides and sulphates. This does not account entirely, however, for the difference between the dry and official methods on the non-tannins from the tannic acid, nor does it in any way account for the difference in the sulphite-cellulose non-tannins, nor for the apparent agreement of the chestnut and clarified quebracho results. The situation here is somewhat similar to the story Mark Twain once wrote in which he placed his characters in all sorts of complex and impossible predicaments and then left it to his readers to untangle the snarls. The fact remains, however, that with practically all of the commercial tanning extracts, the dry method returns results which compare favorably with the official method, notwithstanding the fact that the agreement is brought about by an apparent compensation of errors and, while this is neither a scientifically correct nor chemically legitimate method, the results from Table III seem to show that our official method is not ideal in this respect.

Returning now to the three points which inspired this investigation, we find that the supposition that chromed hide powder acting as a mordant and taking up coloring matter which unchromed hide would not absorb, is subject to some modification, at least as far as its effect on non-tannin results is concerned. Tests were made on hematine and fustic extracts and, notwithstanding the fact that color tests on chrome mordanted wool from the non-tannins showed a greater amount of color remaining in the solutions from the dry method, the non-tannin weights by the official method were invariably higher. This still remains an unsolved problem.

In regard to point No. 2, the advantages of using a dry powder are really the only plausible excuse for the publication of this article. It might be possible, however, to manufacture a powder free from chlorides and of sufficient acidity to meet the demand, which would give chemically legitimate non-tannins and this does not necessarily mean an agreement with the present official method results. However, this is a matter for the hide powder manufacturer.

Concerning point No. 3, that of the nearer approach of laboratory to tannery, the writers would quote from an abstract appearing in the February issue of this JOURNAL entitled "New Methods of Tannin Estimation and Their Practical Value as Compared with the Hide Powder Process," by R. Lauffmann. After criticizing various methods, he reaches the following conclusion: "These methods seem very arbitrary since the adsorbent material is entirely different to hide powder. Errors in the hide powder process are often traceable to fermentation of the liquors or unsuitable treatment of the samples. The great superiority of the hide powder process consists in that *no materials are used either physical or chemical which are not present in the tannery.*"

This, then, is the conclusion of the writers. As a quick alternative method where results are required in a hurry and especially upon samples of unknown approximate tannin content, this procedure is valuable, giving results within the limit of reasonable error. With the aid of Veit's vacuum dryer, results have been obtained in this laboratory within four hours from time of receipt of sample, depending entirely on length of time of filtration of soluble solids solution, which were in practical agreement with the official method results.

THE DETERMINATION OF TOTAL, SOLUBLE AND INSOLUBLE ASH IN LEATHER—COMMITTEE REPORT.

By J. M. Seltzer, Chairman.

The following directions were sent to collaborators:

Do all work in *duplicate.*

Make the following tests on each of samples A and B.

1. *Moisture.*—Dry 10 grams of leather for 16 hours at a temperature between 95°-100° C. (Official method.)

2. *Total Ash.*—Incinerate 10 grams of leather in a tared dish at a dull red heat until all carbon is consumed. If it is difficult to burn off all carbon, treat the ash with hot water, filter through an ashless filter, ignite filter and residue, add filtrate, evaporate to dryness and ignite. (Official method.)

3. *Insoluble Ash.*—After weighing ash in No. 2, add 50 cc. distilled water to the residue in dish and heat on steam bath for 10 minutes, then wash onto ashless filter and wash residue and

paper with hot water until all soluble matter is removed. Ignite filter and residue at a dull red heat and weigh residue which is *insoluble ash.*

4. *Water Soluble Material.*—Digest 30 grams of leather (without removing oil) in a percolator over night (using extraction thimble if possible), then extract with water at 50° C. for 3 hours. The total volume of solution to be 2 liters. Determine total solids by evaporating 100 cc. for 16 hours at 98°-100° C.

5. *Insoluble Ash.*—Remove extracted leather from extraction thimble as obtained in No. 4 and dry 16 hours at a temperature of 98°-100° C., cool and weigh leather. Mix extracted leather thoroughly and take one-third of the weight (equivalent to 10 grams original leather) and place in a tared dish and ignite at a dull red heat until all carbon is consumed. Weigh as *insoluble ash.*

6. *Soluble Ash.*—Evaporate 500 cc. water soluble solution obtained in No. 4 (equivalent to 7½ grams original leather) to small bulk over steam bath, transfer to tared dish rinsing with distilled water and ignite at dull red heat until all carbon is consumed. Weigh as *soluble ash.*

7. *Insoluble Portion of Soluble Ash.*—After having secured the weight of soluble ash in No. 6 add 50 cc. distilled water to the residue in the dish, and heat on steam bath for 10 minutes, then wash onto ashless filter and wash residue and paper with hot water until all soluble matter is removed. Ignite filter and residue at a dull red heat, and weigh residue which is insoluble portion of soluble ash.

Kindly give your comments on the results of your work and your opinion in regard to the most suitable method for determination of total, soluble and insoluble ash.

We would be pleased to have you do any additional work on these samples by any other methods.

The following information was sent out after several of the collaborators' reports were returned:

"Referring to the committee report of total, soluble and insoluble ash in leather we would call your attention to a difficulty which has been experienced in No. 5, insoluble ash. The leather removed from the extraction thimble should be dried at a low temperature before drying at 98°-100°. If this is not done the

LEATHER SAMPLE "A." AIR DRY BASIS.

			Moisture	Ash unextracted leather			Water soluble material	Ash extracted leather				
		Determination	1	2	3	2—3	4	5+6	5	6	7	
	Analyst	Laboratory	Per cent.	Total ash Per cent.	Insoluble ash Per cent.	Soluble ash Per cent.	Per cent.	Total ash Per cent.	Insoluble ash Per cent.	Soluble ash Per cent.	Insoluble portion Soluble ash Per cent.	
1	J. B. Churchill; J. F. Anthes	American Leather Research Laboratory	9.33	1.26	0.81	0.45	30.99	1.31	0.16	1.15	0.49	Used Reed modification water extraction apparatus (glass)
2	W. K. Alsop	Elk Tanning Co.	8.28	1.32	0.85	0.47	27.82	2.19	0.16	2.03	0.79	Copper extractor Alundum thimble
3	S. T. Lowry	Kistler Leather Co.	8.79	1.39	0.77	0.62	28.17	2.26	0.15	2.11	0.61	Copper extractor Copper thimble
4	H. Gordon	Kistler Leather Co.	8.08	1.34	0.82	0.52	30.72	2.13	0.14	1.99	0.70	Copper extractor Copper thimbles
5	F. F. Marshall	Kistler Leather Co.	8.52	1.36	0.86	0.50	30.37	2.24	0.12	2.12	0.60	Copper extractor Copper thimbles
6	E. J. Kern	A. F. Gallun & Sons Co.	11.35	1.34	0.86	0.48	26.16	1.74	0.13	1.61	0.54	Glass extractor
7	F. H. Small; V. J. Mlejnek	Graton & Knight Mfg. Co.	9.61	1.36	0.81	0.55	29.49	1.84	0.13	1.71	0.41	
8	H. L. Riddle	Kistler, Lesh & Co.	9.23	1.36	0.78	0.58	24.49	1.87	0.17	1.70	0.60	
9	R. E. Porter	Ashland Leather Co.	9.13	1.31	0.91	0.40	27.08	1.19	0.11	1.08	0.57	
	Average		9.15	1.34	0.83	0.51	28.37	1.86	0.14	1.72	0.59	
	Maximum		11.35	1.39	0.91	0.62	30.99	2.26	0.17	2.12	0.79	
	Minimum		8.08	1.26	0.77	0.40	24.49	1.19	0.11	1.08	0.41	
	Greatest difference		3.27	0.13	0.14	0.22	6.50	1.07	0.06	1.04	0.38	

LEATHER SAMPLE "A." ABSOLUTELY DRY BASIS.

			Moisture	Ash unextracted leather			Water soluble material	Ash extracted leather				
		Determination	1	2	3	2—3	4	5+6	5	6	7	
	Analyst	Laboratory	Per cent.	Total ash Per cent.	Insoluble ash Per cent.	Soluble ash Per cent.	Per cent.	Total ash Per cent.	Insoluble ash Per cent.	Soluble ash Per cent.	Insoluble portion Soluble ash Per cent.	
1	J. B. Churchill; J. F. Anthes	American Leather Research Laboratory	0.00	1.39	0.89	0.50	34.17	1.44	0.17	1.27	0.54	Used Reed modification water extraction apparatus (glass)
2	W. K. Alsop	Elk Tanning Co.	0.00	1.43	0.92	0.51	30.32	2.38	0.17	2.21	0.86	Copper extractor Alundum thimble
3	S. T. Lowry	Kistler Leather Co.	0.00	1.52	0.84	0.68	30.89	2.48	0.17	2.31	0.67	Copper extractor Copper thimble
4	H. Gordon	Kistler Leather Co.	0.00	1.46	0.89	0.57	33.42	2.32	0.15	2.17	0.76	Copper extractor Copper thimbles
5	F. F. Marshall	Kistler Leather Co.	0.00	1.48	0.94	0.54	33.21	2.45	0.13	2.32	0.66	Copper extractor Copper thimbles
6	E. J. Kern	A. F. Gallun & Sons Co.	0.00	1.51	0.97	0.54	29.51	1.96	0.15	1.81	0.61	Glass extractor
7	F. H. Small; V. J. Mlejnek	Graton & Knight Mfg. Co.	0.00	1.50	0.90	0.60	32.62	2.03	0.14	1.89	0.45	
8	H. L. Riddle	Kistler, Lesh & Co.	0.00	1.49	0.86	0.63	26.97	2.05	0.18	1.87	0.66	
9	R. E. Porter	Ashland Leather Co.	0.00	1.44	1.00	0.44	29.78	1.31	0.12	1.19	0.63	
	Average		0.00	1.47	0.91	0.56	31.21	2.05	0.15	1.90	0.65	
	Maximum		0.00	1.52	1.00	0.68	34.17	2.48	0.18	2.32	0.86	
	Minimum		0.00	1.39	0.84	0.44	26.97	1.31	0.12	1.19	0.45	
	Greatest difference		0.00	0.13	0.16	0.24	7.20	1.17	0.06	1.13	0.41	

LEATHER SAMPLE "B." AIR DRY BASIS.

			Moisture	Ash unextracted leather			Water soluble material	Ash extracted leather				
		Determination	1	2	3	2—3	4	5+6	5	6	7	
	Analyst	Laboratory	Per cent.	Total ash Per cent.	Insoluble ash Per cent.	Soluble Per cent.	Per cent.	Total ash Per cent.	Insoluble ash Per cent.	Soluble ash Per cent.	Insoluble portion Soluble ash Per cent.	
1	J. B. Churchill; J. F. Anthes	American Leather Research Laboratory	9.05	1.31	0.81	0.50	32.78	1.31	0.19	1.12	0.50	Used Reed modification water extraction apparatus (glass)
2	W. K. Alsop	Elk Tanning Co.	8.18	1.33	0.80	0.53	31.62	2.25	0.14	2.11	0.57	Copper extractor Alundum thimble
3	S. T. Lowry	Kistler Leather Co.	8.35	1.35	0.80	0.55	32.80	2.04	0.13	1.91	0.55	Copper extractor Copper thimble
4	H. Gordon	Kistler Leather Co.	8.04	1.35	0.78	0.57	32.94	2.11	0.13	1.98	0.52	Copper extractor Copper thimbles
5	F. F. Marshall	Kistler Leather Co.	8.56	1.35	0.81	0.54	32.45	1.96	0.13	1.83	0.57	Copper extractor Copper thimbles
6	E. J. Kern	A. F. Gallun & Sons Co.	11.17	1.33	0.81	0.52	29.13	1.69	0.11	1.58	0.59	Glass extractor
7	F. H. Small; V. J. Mlejnek	Graton & Knight Mfg. Co.	9.22	1.34	0.78	0.56	31.75	1.77	0.12	1.65	0.38	
8	H. L. Riddle	Kistler, Lesh & Co.	8.94	1.37	0.78	0.59	28.60	1.73	0.13	1.60	0.55	
9	R. E. Porter	Ashland Leather Co.	8.80	1.30	0.91	0.39	30.15	1.15	0.13	1.02	0.44	
	Average		8.92	1.33	0.81	0.52	31.36	1.78	0.13	1.65	0.52	
	Maximum		11.17	1.37	0.91	0.59	32.94	2.25	0.19	2.11	0.59	
	Minimum		8.04	1.30	0.78	0.39	28.60	1.15	0.11	1.02	0.38	
	Greatest difference		3.13	0.07	0.13	0.20	4.34	1.10	0.08	1.09	0.21	

LEATHER SAMPLE "B." ABSOLUTELY DRY BASIS.

			Moisture	Ash unextracted leather			Water soluble material	Ash extracted leather				
		Determination	1	2	3	2—3	4	5+6	5	6	7	
	Analyst	Laboratory	Per cent.	Total ash Per cent.	Insoluble ash Per cent.	Soluble ash Per cent.	Per cent.	Total ash Per cent.	Insoluble ash Per cent.	Soluble ash Per cent.	Insoluble portion Soluble ash Per cent.	
1	J. B. Churchill, J. F. Anthes	American Leather Research Laboratory	0.00	1.44	0.89	0.55	36.04	1.44	0.21	1.23	0.56	Used Reed modification water extraction apparatus (glass)
2	W. K. Alsop	Elk Tanning Co.	0.00	1.45	0.87	0.58	34.43	2.45	0.15	2.30	0.62	Copper extractor Alundum thimble
3	S. T. Lowry	Kistler Leather Co.	0.00	1.47	0.87	0.60	35.79	2.22	0.14	2.08	0.60	Copper extractor Copper thimble
4	H. Gordon	Kistler Leather Co.	0.00	1.47	0.85	0.62	35.82	2.30	0.14	2.16	0.57	Copper extractor Copper thimbles
5	F. F. Marshall	Kistler Leather Co.	0.00	1.48	0.89	0.59	35.49	2.14	0.14	2.00	0.62	Copper extractor Copper thimbles
6	E. J. Kern	A. F. Gallum & Sons Co.	0.00	1.49	0.91	0.58	32.79	1.90	0.12	1.78	0.66	Glass extractor
7	F. H. Small, V. J. Mlejnek	Graton & Knight Mfg. Co.	0.00	1.47	0.86	0.61	34.98	1.95	0.13	1.82	0.41	
8	H. L. Riddle	Kistler, Lesh & Co.	0.00	1.50	0.85	0.65	31.40	1.89	0.14	1.75	0.60	
9	R. E. Porter	Ashland Leather Co.	0.00	1.42	1.00	0.42	32.95	1.26	0.13	1.13	0.49	
	Average		0.00	1.47	0.89	0.58	34.41	1.95	0.14	1.81	0.57	
	Maximum		0.00	1.50	1.00	0.65	36.04	2.45	0.21	2.30	0.66	
	Minimum		0.00	1.42	0.85	0.42	31.40	1.26	0.12	1.13	0.41	
	Greatest difference		0.00	0.08	0.15	0.23	4.64	1.19	0.09	1.17	0.25	

leather will char to such an extent that it will be impossible to obtain an accurate portion for the insoluble ash."

Two samples of prepared leather marked "A" and "B" were sent to each collaborator. The samples were cut with a machine consisting of four 10-inch rip saws clamped together and run at a speed of 2,400 revolutions per minute. Each sample was thoroughly mixed and placed in a sealed glass jar in order to give each collaborator uniform samples.

The Epsom salts ($MgSO_4.7H_2O$) in these leathers was found to be as follows:

	Air dry basis Per cent.	Absolutely dry basis Per cent.
Sample A	3.72	4.05
Sample B	3.54	3.86

The results found by those co-operating are shown in the following tables.

All results are the average of duplicate analyses.

COMMENTS.

J. B. CHURCHILL AND J. F. ANTHES:

1. *Moisture.*—Ten grams of leather dried for 16 hours in Alsop evaporator.

2. *Total Ash.*—Ignitions made in platinum dishes.

3. *Insoluble Ash.*—As No. 2.

4. *Water Soluble Matter.*—For this determination the Reed modification of extractor was used. This consists essentially of a set of glass tubes about 1½ inches in diameter and 10 inches long placed in the water bath about 15 inches in diameter and 15 inches high. A plug of cotton is placed in the bottom of the tube and the leather packed on the cotton. Another layer of cotton is then placed above the leather. The tubes are then placed in the water bath and the leather covered with water, allowed to soak over night. The bath is then filled with distilled water and brought to 50°. Percolation is then started; the water entering the tubes through a one-hole No. 9 rubber stopper. An air space is always maintained between the leather and the stopper, closing the tube.

As I have written a description of this apparatus for Mr. Alsop, and it will be published in the April JOURNAL, I will not go into further details. You may find the results for water soluble slightly higher than those obtained by the Oberfell type of extractor. Otherwise the method is the same as the official.

5. *Insoluble Ash.*—This determination was carried out exactly in accordance with your directions with the exception of this modification. The leather obtained from the water extraction was dried and 10 grams of the absolutely dried leather ashed and the value calculated back to the original leather. Ignitions in platinum.

6. *Soluble Ash.*—Exactly in accordance with your directions. Ignitions in platinum.

7. After determining the insoluble ash, we have determined the portion of insoluble, in water, following out the detail which you give for the determination of insoluble ash under No. 3.

This work was carried out by myself and my assistant, Mr. J. F. Anthes.

In response to your request for my opinion as regards the best method of determining total, insoluble and soluble ash I will make the following comments:

1. Referring by number to the determinations as listed in table of results.

2 and 3. *Total Ash.*—I believe that this value will vary somewhat according to the temperature at which the ignitions are made and whether or not the ignitions are made in porcelain or platinum. In a leather containing magnesium sulphate, there is a certain portion of the sulphuric acid driven off by heating. Just how much I do not know. This loss renders a certain portion of the ash insoluble that would otherwise be soluble. For this reason I believe that the determination of insoluble and soluble ash according to method No. 3 of your directions is absolutely unreliable and that the figures given under No. 7 in table of results point very definitely to this conclusion.

For the determination of insoluble ash, I believe that the best method is that given in paragraph No. 5 of your directions, namely: to ignite a portion of the leather which has been dried

after the extraction of the water soluble matter. The difference between this value and the total ash will be sufficiently accurate to accept as a value for the soluble ash.

If it is desired to obtain a direct figure for the percentage of soluble ash, the method given by you in your directions under paragraph No. 6 should be used.

W. K. ALSOP:

1. *Moisture.*—Samples were dried as you specified in an evaporator and drier.

2. *Total Ash.*—It is quite possible to vary considerably the percentage of ash found in some leather, especially those containing Epsom salts.

3. *Insoluble Ash.*—The total ash was treated as you directed and washed on the filter with about 150 cc. of hot water.

4. *Water Soluble Material.*—Our extractor for this purpose is made of copper, but the leather is in an alundum thimble.

5. *Insoluble Ash.*—The method you give is not practicable unless the extracted leather is dried at a low temperature before drying at 98°. I ashed the whole amount of leather equivalent to 30 grams.

6. *Soluble Ash.*—Was determined as directed.

7. *Insoluble Portion of Soluble Ash.*—Was determined as requested in your letter of the 31st. This ash contained copper probably a small amount and I did not determine it. I have noticed this before where copper extractor is used. I have come to the conclusion that copper should not be used for extracting water solubles in leather and am going to change mine so that the leather will not come in contact with anything but glass.

ERWIN J. KERN: The wide discrepancies between the results given by the alternative methods are easily explained. Analysis of the water soluble matter from both leathers shows the presence of the sulphates of iron, aluminum, calcium, and magnesium. By procedure No. 2 for determining the total ash, it is almost impossible to prevent a reduction of the sulphates during ashing, because of the large amount of organic matter present. By calculating the total ash from procedures No. 5 and No. 6, a much higher result is obtained, evidently because the soluble portion contained nearly all of the sulphates, which were ashed in the

presence of much less organic matter than in the case of procedure No. 2, and consequently suffered less reduction. The higher figures, therefore, are probably more nearly correct.

By reduction of the sulphates in the ashing of the original leather, much of what would have been soluble ash is rendered insoluble. For example, magnesium sulphate, which is very soluble, becomes practically insoluble when reduced to the oxide. It is no wonder, then, that the insoluble ash as determined by procedure No. 3 is much greater than that by procedure No. 5. For the same reason we should expect procedure No. 6 to give a higher result for soluble ash than that calculated from procedure No. 2 and No. 3.

Upon digesting the soluble ash from procedure No. 6 with water, a large portion was found to have become insoluble, suggesting a considerable amount of reduction, even in this determination. This would indicate that even the higher values for both soluble and total ash are still short of the true values. The two leathers you sent represent, of course, only one type of leather, the difficulties with which may be very different from those of other types.

VINCENT J. MLEJNEK: In looking over the figures, one is struck by the wide discrepancy between the soluble and insoluble ash as found by the two methods. In fact, the soluble ash as found in No. 6 is much greater than the total ash in the leather as found in No. 2. Obviously something occurs either in the direct ashing in No. 2, or during the water extraction as found in No. 4. To my mind, the most plausible explanation of this fact is that in the direct ashing for total ash, the large amount of carbon present reduces the salts contained in the leather to oxides, whereas the relatively small amount of carbon encountered in No. 6 has no such marked reducing effect. That is to say, the ash in No. 6 contains the salts practically in their original form. This reasoning would tend to show that No. 6 is a much truer figure than No. 2, which I believe is so.

In No. 3 the effect of the reduction in No. 2 is shown in a high insoluble ash figure, due, no doubt, to the reduction of sulphates, and other soluble salts into insoluble oxides. No. 5 shows the true insoluble ash, because it is the ash of all the leather sample which was insoluble in H_2O.

A really valuable ash figure, it seems to me, would consist of 5 and 6, No. 5 showing the ash of the matter soluble in water with a minimum of salt reduction, and No. 6 showing the ash of the matter not soluble in water, which being so small in the total cannot be greatly varied by the reduction of the carbonizing leather substance.

If it is desired to get a line on the bases constituting the ash, and no special importance is attached to the acid radicals of the salts, ashing in the presence of H_2SO_4 or reheating the ash with the addition of H_2SO_4, thus converting the bases into sulphates, would do away with the reduction of the ash salts to oxides and give an ash figure in a way comparable with the figure obtained in No. 5 and No. 6.

It would also make for more concordant results between different laboratories on the ash figure, since the amount of reduction in ashing would probably be different with different operators.

HARRY GORDON: In the case of determination No. 5, I dried the extracted leather very slowly on the steam bath, but the leather charred, so therefore I did not dry it in the oven as called for by the method, but placed it under the steam bath until the substance was dry enough to ash. I did not meet with any difficulties in ashing the entire extracted sample this way.

In making determinations No. 2 and No. 6, I noticed that more heat was required to burn off all the carbon in No. 2 than in No. 6. The latter ashed without any trouble. I think that the discrepancy in the percentages of "total ash" by method No. 2 and No. 6 is due to this excessive heat required to ash the leather by method No. 2 and also probably due to the fact that the same sample as ashed by method No. 2 contained more carbon than the sample ashed by method No. 6.

I determined the water soluble of the leather in a copper extractor and thimble and I, therefore, analyzed the insoluble part of the soluble ash for copper which I found to be 0.14 per cent. by the iodimetric method.

Before analyzing the insoluble portion of the soluble ash for copper it occurred to me that possibly the difference in ashes between No. 2 and No. 6 was due to the copper from the ex-

tractor and the thimble, but the percentage of copper found was small in comparison to the differences. The discrepancy between the two methods is, therefore, probably due to other sources as stated above.

My conclusions are that methods No. 2 and No. 5 should be used to determine the total ash and the insoluble ash respectively and the soluble ash taken by the difference between the total and the insoluble ash as determined above.

F. F. MARSHALL: It is the writer's opinion that the most satisfactory method for determining the insoluble ash is by method No. 5, ashing the leather remaining from the water soluble extraction. The soluble ash would be the difference between the total ash and the insoluble ash.

The instructions of the Chairman were carried out with but one exception, No. 5, insoluble ash.

The total remaining leather from the water soluble extraction was slowly dried in a current of warm air to approximately 5 per cent. moisture, it was then thoroughly mixed. There was no charring and no hard lumps formed.

Sample "A"—One-third of the total remaining leather from the water soluble extraction was ashed.

Sample "B"—The total remaining leather from the water soluble was ashed.

The water soluble was made in a copper extractor with copper thimbles.

Platinum dishes were used throughout for the ignitions.

CHAIRMAN: There is an apparent difference in the total ash by the two methods used by this Committee and it is evident that ashing the leather direct gives a lower total ash than when the ash is determined from the water soluble solution and extracted leather. It is the opinion of most of the collaborators that when the ash is determined direct the excess of carbon causes a reduction of the salts converting them into oxides; these oxides are insoluble in water and this is the cause for the high percentage of insoluble ash formed when determining the ash direct and dissolving the ash in water and also for the large

amount of insoluble ash formed in the water soluble material ash after ignition.

Insoluble Ash.—Method No. 3 is not satisfactory for determining the insoluble ash and this experiment was performed to show that such was the case. Method No. 5 is satisfactory for insoluble ash, but the water-extracted leather should be slowly dried before drying at the higher temperature in order to avoid charring.

Total Ash.—There may be some difference of opinion regarding the method for determining total ash; if the present method is changed it will cause all figures secured in the past to be out of comparison with those secured by adding the soluble ash from water soluble extraction solution and the insoluble ash from water-extracted leather. Some collaborators favor this latter method and believe that it more nearly represents the mineral matter present in the leather. It is doubtful whether more information could be secured by this method than the ash determined directly, as in neither case does the total ash figure show true values. Leather A contained 4.05 per cent. $MgSO_4.7H_2O$ and total ash direct was 1.47 per cent., while total ash from extraction method was 2.05 per cent. Leather B contained 3.86 per cent. $MgSO_4.7H_2O$ and total ash direct was 1.47 per cent., while total ash from extraction method was 1.95 per cent. It is apparent that neither method above gives true mineral values and only arbitrary figures.

Recommendations: Insoluble Ash.—Digest and extract 30 grams of leather in an extraction thimble placed in a water extraction thimble placed in a water extraction apparatus as described under official method for water soluble materials. Remove the extracted leather from the thimble and dry slowly at a low heat after which dry 16 hours at a temperature of 98°-100°, cool and weigh leather. Mix extracted leather thoroughly and take one-third of the weight (equivalent to 10 grams original leather) and place in a tared dish and ignite at a dull red heat until all carbon is consumed. Weigh as *insoluble ash.*

Total Ash, Soluble Ash.—I suggest that this matter be discussed by the Association in order to determine what is desired and how the total ash figure will be used in reporting the analysis of leather.

PHYSIOLOGICAL RESEARCHES ON A NEW SURFACE YEAST GROWING ON TAN-LIQUORS.*

By T. Asai.

Journal of the College of Science, Imperial University of Tokyo, Vol. 39, No. 7, May 30, 1918.
Abridged translation by Dr. Lloyd Balderston.

The activities of various kinds of micro-organisms are concerned in the processes of leather manufacture. The bacteria and bacterial products which are active in the soaks, in the sweating process, in the limes and in puers or bates have been extensively studied.[1] Not only the activities of bacteria, but also those of yeasts and moulds are concerned in the various processes of the tannery. Andreasch found that yeasts produce CO_2 and alcohol and also the three acids, acetic, lactic and butyric. The presence of acetic and lactic acids in the earlier stages of the tanning process is beneficial because of their swelling effect on the hide fiber. It is well known that the acetic acid fermentation of alcohol is set up by the products of certain yeasts. According to Eitner (*Handbuch der tech. Mycologie,* Vol. 5, p. 30), tan liquors as a rule do not contain more than 2 per cent. of alcohol; in a few abnormal cases as much as 3 per cent.

The yeasts which grow most abundantly in the tan-vats are *Sacchiromyces Pastorianus, S. ellipsoideus, S. apiculatus,* and some torulas, including an orange yellow one and the kinds called "rose yeasts." Besides these there are species of *mycoderma* which make a little acetic acid in the liquors, but only when they are at rest. In general, mycoderma are harmful, because they destroy not only alcohol and organic acids, but also tannin, as do some moulds. A further damage discovered by Eitner on the surface of a sample of sole leather tanned with Australian wattle bark consisted of dark brown or black indelible spots, due to a kind of mycoderma.

The author found in the Senju tannery of the Japan Hide & Leather Co. a species of mycoderma which makes indelible dark

* Translated for the JOURNAL of the American Leather Chemists Association.

[1] The author refers to the work of Andreasch and to articles by Eitner, but seems not to be familiar with the work of Popp and Becker, J. T. Wood, Röhm, etc.—TRANSLATOR.

brown spots, which, although only surface discolorations, are not removable by acids nor bleaching agents. In old liquors a heavy growth of this mycoderma takes place, and after 3 or 4 weeks a thick red-brown skin may be seen on the undisturbed liquor. Injury from the spots is greatest in the hot, rainy months of June and July, that is, during the time of year most favorable for the growth of moulds and yeasts. It is not unusual for sole leather when taken out of such liquors and laid in pile to become infected by this mycoderma and seriously injured in the course of a few days. The growth of this organism was first noticed some years ago, and the damage from it has been increasing.

The cells of the organism are long or ellipsoidal, sometimes half-moon shaped, 3.2 to 4μ wide and 8 to 11μ long. Each cell generally contains two or three highly refractive bodies, attached to the cell-wall or in the vacuole. Besides these there are occasionally observed two or three, less often four, oil droplets, similar to the "ascospores" of the saccharomycetes, giving the well-known reaction with osmic acid and easily soluble in alcohol. These occur especially abundant in the cells of specimens grown in yeast-extract. (Fig. 2.)

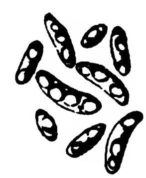

FIG. 2.—Cells with spore like fat droplets from a film on yeast-extract, 7 days old, at 28-30° C. Magnification 1,200.

Reproduction takes place by budding, not by spores. After a few weeks, however, a culture on a piece of gypsum or on leather will develop, if kept at 30° to 35° C., special cells, round in outline, from 7.3 to 9.7μ in diameter, with thick cell-membranes. These have no vacuoles and are full of glycogen and fat-droplets. They are "endurance cells," such as are often observed in the case of bottom yeasts. In old cultures the occurrence of nearly round cells with heavy walls is not unusual.

The large colony, plate 1, Fig. 1, grew on soy agar,[2] at 28° C., in a few days to nearly full size. It was grayish white, net-like in the middle, radially folded at the edge, which is irregularly

[2] Soy culture medium is made as follows: tap water, 800 cc.; cane sugar, 50 grams; onion juice, 100 cc.; commercial soy, 50 cc. Soy is a sauce made in Japan from the soy bean. Soy agar is prepared as above with addition of 20 grams agar.

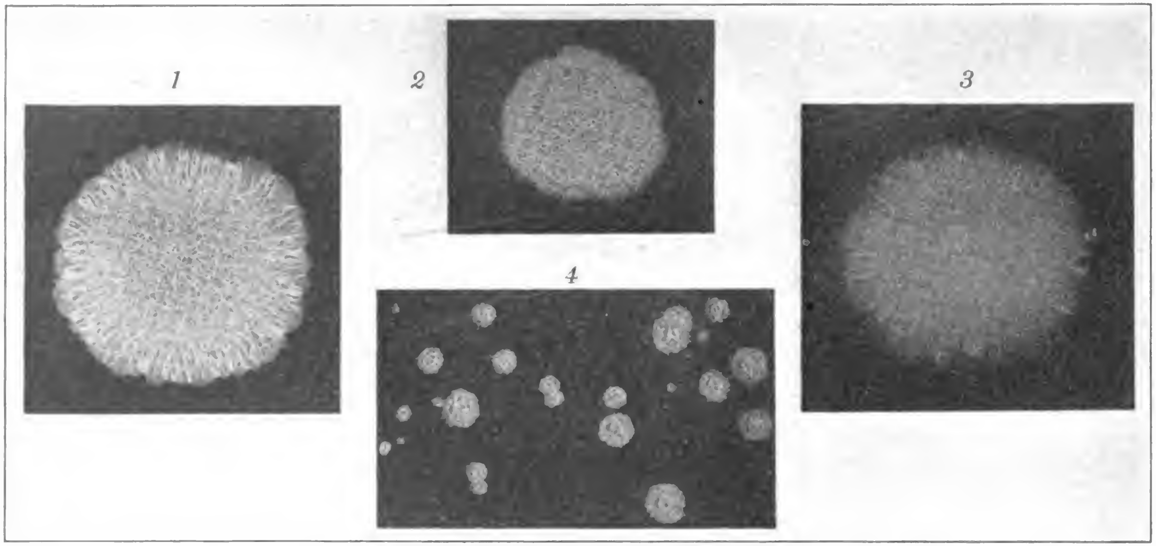

FIG. 1.—Large colony of M. tannica at 28° on soy agar after one day. Natural size.
FIG. 2.—The same on yeast-extract agar.
FIG. 3.—The same on wort-agar.
FIG. 4.—Colonies from single cells of M. tannica at 28° on soy-agar after 24 hours. Natural size.

toothed. The small colonies from single cells, plate 1, Fig. 4, show already in 24 hours an irregular appearance, deep in the center and folded. On yeast-extract[3] agar, the colony, plate 1, Fig. 2, shows thick, white, net-like folds, and at the edge a raised ring-fold, to which after a few days one or more others were added. The colony on wort-agar, plate 1, Fig. 3, spread out rather thin, with numerous fine radial folds on the surface. On the edge, this colony was smooth, without folds.

Grown in the liquid medium made with soy, the organism covered the whole surface of the liquid in 24 hours with a heavy, folded, gray-white skin, which in a week mostly fell to the bottom, as a heavy flocculent precipitate, the solution becoming cloudy. On the surface a thin non-folded residue remains. The dry weight of this material growing in one week in a 150 cc. flask with 30 cc. of culture liquid was 0.176 gram. Yeast-extract (Koji) is the best medium in this series, the skin being strongly folded in waves, as on soy, and even thicker. Here also at the end of a week all but a thin residue had been precipitated. The weight of dry material in this case was 0.264 gram. The skin formed on wort was thin and finely folded, weighing 0.122 gram.

The micro-organisms existing in the tan-liquors derive the necessary nourishment from the tannin, the so-called non-tannins of the tanning material and from the hide-substance. As a source of carbon the non-tannins are most important, but a few kinds of yeasts attack tannin also. Nitrogen is furnished by the hide, and also by some substances derived from the tanning materials. Among available materials in the non-tannins, Andreasch has pointed out as carbon sources, dextrose, laevulose, invert sugar and cane sugar, and as sources of nitrogen, albumoses, peptones, etc. For some micro-organisms, especially mycoderma, other transformation products in the liquors, as alcohols and some organic acids, serve as nutrient materials.

In order to test the assimilation of various substances by the particular mycoderma under discussion, the author made series of solutions in the manner following. The substances to be tested as sources of carbon were made into 3 per cent. solutions with distilled water, each solution containing beside the 3 per cent. of

[3] This medium is made with "koji," a commercial product, the manufacture of which involves treatment of cooked rice with a yeast.

material to be tested as a source of carbon, 1 per cent. of ammonium sulphate to supply nitrogen, and 1/5 per cent. each of magnesium sulphate and monopotassium phosphate. These are designated as "culture solution I." The materials to be tested as sources of nitrogen were in a similar way introduced to the amount of 1 per cent. into solutions also containing 3 per cent. of grape sugar and 1/5 per cent. each of magnesium sulphate and monopotassium phosphate. Such media are called "culture solution II." Thirty cubic centimeters of the medium to be tested were placed in a 150 cc. Erlenmeyer, the flask plugged with cotton and sterilized in steam. Each was inoculated with a small quantity of pure culture of the mycoderma, taken from soy agar and incubated for a week at 27° to 30° C. The growth was collected on a tared filter, washed, dried and weighed. The weight so obtained was taken as a measure of the nutrient value of the substance in question. It is well known that as a source of carbon for the nutriment of yeasts, the carbohydrates are most favorable. The author gives detailed results of tests as outlined above on various carbohydrates. The amounts of dry yeast cells from these tests were as follow: (milligrams), glucose 111, levulose 96, mannose 92, galactose 22, cane sugar 72, maltose 21, lactose 21, raffinose 28, dextrin 22, inulin 17, glycogen 20. Methyl alcohol and amyl alcohol, tested in the same manner, gave no growth. Ethyl alcohol yielded 47 milligrams, glycerine 12 and mannite 14. Methyl alcohol was tested in smaller percentages, and up to 1 per cent. gave some growth. Ethyl alcohol was tested in various strengths from 0.1 to 10 per cent. The largest yield was from a 1 per cent. solution, 78 milligrams. With larger percentages the yield decreased, until in the 10 per cent. solution there was only a very slight growth. Amygdalin and salicin, tested in 3 per cent. solution, gave small yields. Tannin gives no growth in 3 per cent. solution, but 9 milligrams in 0.1 per cent. solution and 15 milligrams in 0.05 per cent. solution were obtained. Gallic acid is able to furnish carbon, and when tannase is formed in a tannin solution by the action of mould or yeast, the gallic acid produced by the action of the tannase in splitting up tannin permits a considerable growth in the presence of rather high percentages of tannin. Potassium salts of organic acids were tested as sources of carbon. The lactate gave, in the stand-

ard conditions described above 30 milligrams of dry yeast, the tartrate 23, malate 13, acetate 12, benzoate 9, and the following five none: formate, oxalate, citrate, butyrate, succinate.

In making the tests as described above for determining the availability of various substances as sources of nitrogen, not only are the weights of dry material grown under the standard conditions given, but also the percentages of the nitrogen present in the culture solution used up by the growth of the organism are calculated. The nitrogen content of the dry cells of the mycoderma, from the average of several determinations, was 6.6 per cent. Alkaline nitrates and nitrites were found not available as sources of nitrogen. In all cases ammonium compounds give good yields. In each of the following cases, the first figures give weight of dry cells, the percentage which follows being as explained above the percentage of all nitrogen present in the solution which was used up during the week's growth. Ammonium carbonate, 21, 1.88 per cent.; chloride, 65, 5.46 per cent.; nitrate, 56, 7.04 per cent.; phosphate, 64, 11.55 per cent. sulphate, 112, 11.62 per cent.; oxalate, 150, 14.61 per cent.; tartrate, 131, 18.93 per cent. Of the organic substances tested, oxamid and benzamid gave no growth. Others were as follow: acetamid, 1.09, 10.11 per cent.; succinimid, 53, 9.74 per cent.; urea, 56, 2.64 per cent.; biuret, 85, 4.59 per cent.; glycocoll, 125, 14.73 per cent.; alanin, 173, 24.18 per cent.; tyrosin, 106, 30.13 per cent.; asparagin, 129, 26.76 per cent.; asparagin acid, 1.57, 32.79 per cent.; peptone, 128.

The fermentive power of the mycoderma toward various sugars was tested qualitatively with the following results: positive, glucose, levulose, mannose, maltose, saccharose, raffinose, α-methylglucoside; negative, galactose, lactose, dextrin, inulin. Quantitative tests were made on glucose, levulose, cane sugar (saccharose), maltose and raffinose, using solutions containing 5 per cent. of the sugar to be tested, 1 per cent. of asparagin and ¼ per cent. each of magnesium sulphate and monopotassium phosphate; 20 cc. of such a solution being placed in a Lindner's flask. After the medium was sterilized, the cotton plug was replaced by a Buchner's valve, and the flask inoculated with the organism, from a two days' culture on soy agar. The flask was now weighed and incubated for 6 hours at 27° to 28° C. The flask was now weighed again and then incubated for 18 hours more

and again weighed. For camparison, a flask with glucose medium and brewer's yeast was run at the same time. The loss in weight of the culture flask was taken as a measure of the amount of CO_2 evolved. The flask with brewers' yeast lost 93 milligrams in 6 hours, and 307 in 24 hours. The figures in milligrams for the several sugars fermented with the mycoderma follow, the first number being in each case the loss in 6 hours, and the second the loss in 24 hours: glucose, 14, 17; levulose, 13, 15; saccharose, 12, 14; maltose, 12, 12; raffinose, 12. 12.

Formation and Destruction of Acid.—The production of acids in the tan-liquors depends on the activities of a series of bacteria and yeasts, and upon the preliminary alcoholic fermentation. This mycoderma does not produce alcohol nor acetic acid in noticeable quantities, nor lactic acid at all. It does, however, as has been shown, assimulate both acids and alcohol as sources of carbon, so it is the reverse of useful in the leather-making process. This organism also produces oxalic acid in the liquors, which is a disadvantage both directly because this acid injures the leather and indirectly because it hinders the fermentations which produce useful materials. To determine the production of acid, culture media were made up with 2 per cent. of grape sugar, cane sugar or alcohol as the source of carbon, 1 per cent. of ammonium sulphate, asparagin, peptone or ammonium tartrate as the source of nitrogen. The largest production of volatile acid was about 0.01 per cent., estimated as acetic. Some combinations made only a trace of non-volatile acid. The largest yields were with grape sugar and ammonium sulphate or tartrate, about 0.2 per cent. estimated as oxalic acid. Alcohol and ammonium tartrate gave 0.12 per cent. The period of incubation was 3 weeks.

The action of the mycoderma as a destroyer of acids was tested by preparing culture media having no source of carbon except the acid, and also with media having beside the acid a good source of carbon. In the former case, a solution having 1 per cent. of acetic acid gave no growth of the organism. Solutions with 0.5 and 0.1 per cent. gave considerable growths in 10 days, using up two-thirds of the acid in the former case and one-fourth of it in the latter. In the presence of a good source of carbon, there was also no growth on a 1 per cent. solution, while the

percentages used up from 0.1 and 0.5 per cent. solutions were somewhat larger than in the previous case, about three-fifths and four-fifths respectively. Similar tests with lactic acid gave almost nothing when no source of carbon was added. In the presence of a source of carbon the organism flourished when the percentages of lactic acid were from 0.1 to 3 per cent., the percentage of acid used up in 10 days rising as the total acid increased, the greatest being 60 per cent.

Influence of Tannin on the Growth.—In general, tannin is not available as nutriment for micro-organisms, repressing the fermentations and hindering the growth of the cells. It has been shown that the alcoholic fermentation of fruit juices is hindered by the presence of tannin in them, and that the growth of the apiculatus yeast is also checked by it. According to Bokorny tannin in even small amounts (0.5 to 1 gram), suffices to kill 10 grams of fresh pressed yeast. He has shown that 1 per cent. tannin kills infusoria instantly, and 0.1 per cent. after a few minutes. The cause of this poisonous effect seems to be the partial precipitation of the albuminous materials which are present in the structure of the micro-organisms. Gallic acid, a decomposition product of tannin, which does not form compounds with albumin, does not hinder the growth of micro-organisms, but often serves as a source of carbon in nutrient liquids.

Researches by Fischer and Freudenberg have shown that tannic acid is related to the sugars, and in many respects a compound synthesized from 5 molecules of digallic acid and 1 of glucose resembles tannin. Pure tannin on hydrolysis yields from 5 to 7 molecules of glucose. The hydrolysis of tannin is not affected simply by boiling with dilute sulphuric acid. It requires enzymatic action, as was first shown by Scheele. When tannin has been split by this enzyme (tannase), it may serve as a source of carbon for the nourishment of micro-organisms. Fernbach and Pottevin have shown the production of tannase by *Aspergillus niger* and *Penicillium glaucum*. Knudson reports that of 28 moulds examined by him, only *Aspergillus niger, A. flavus* and a species of *Penicillium* were able to endure the addition of 10 per cent. of tannin to bean extract. He has also shown that *Aspergillus niger* and the *Penicillium* could use tannin as the sole source of carbon. Production of tannase is not limited to

these moulds. According to Meissner there is a sort of *Mycoderma* which can split tannin.

To determine the influence of tannin on the growth of the organism under investigation, a series of cultures was made containing 3 per cent. of glucose as the source of carbon, and different materials as sources of nitrogen. To these were added varying percentages of tannin, and they were inoculated with the organism. In the series having ammonium sulphate as the source of nitrogen, no growth occurred on the flask having 1 per cent. of tannin. That with 0.5 per cent. produced 67 milligrams of growth, that with 0.1 per cent., 121 milligrams, and the control, with no tannin, 101 milligrams. In the series with ammonium tartrate, the control produced 133 milligrams, that with 0.1 per cent. tannin 147, that with 0.5 per cent., 241, that with 1 per cent., 233, and that with 2 per cent. tannin no growth at all. When asparagin was used as the source of nitrogen, the cultures having up to 5 per cent. tannin showed growth. The figures follow: no tannin, 112 milligrams; 0.1 per cent., 159 milligrams; 0.5 per cent., 237 milligrams; 1 per cent., 244 milligrams; 2 per cent., 281 milligrams; 3 per cent., 412 milligrams; 4 per cent., 275 milligrams; 5 per cent., 154 milligrams.

Production of Tannase.—The utilization of tannin as nutriment by this organism, which as a new species has been named *Mycoderma tannica,* must be due to the splitting of the tannin by enzymatic action into simpler materials, which may serve as nutriment, since tannin itself is poisonous to micro-organisms generally. Researches on the fermentation of tannin have been conducted by Knudson and others, these being confined, however, to a few moulds. The availability of gallic acid as a nutrient material was abundantly demonstrated.

To test the power of *M. tannica* to produce tannase, a dry preparation was made according to the method of Lebedew. A week-long growth was made on culture solution I (glucose as source of carbon) and various tannin percentages. The growth was taken off, washed, dried for two days in an incubator at 35° C., and the dry powder used as inoculation material. Of this dry material, 0.3 gram was added to 50 cc. tannin solution, with 1 per cent. toluol, and incubated for a week at 35° C. Afterward the remaining tannin was estimated by Jean's method

(*Chem. Centralbl.*, 1900, pp. 1107-8). The loss of tannin is taken as a measure of the production of tannase. The amount of tannin in each 50 cc. of solution at the start was 176 milligrams. In that which had been inoculated with powder from a culture medium containing no tannin, the loss of tannin in one week was 61 milligrams, nearly 35 per cent.; the loss in the solution inoculated from a culture on 0.1 per cent. tannin solution was 41 per cent.; in that whose inoculation was from a 0.5 per cent. tannin solution, 51 per cent. This was the maximum loss, corresponding to the greatest tannase content. The tannin solutions inoculated from 1, 3 and 5 per cent. tannin-content culture media suffered losses of 31, 21 and 7 per cent. respectively.

Mycoderma Spots on Sole Leather.—Eitner's observation on spots due to micro-organisms have been referred to above. These are caused by the presence of the actual material of the organism imprisoned among the fibers of the leather. It was specially emphasized that these spots only occurred on leather which had been tanned with mimosa bark (wattle) and that the use of this material was in some way related to the development of the spots. Eitner, therefore, called them "mimosa stains." The stains observed in the Senju tannery as above mentioned, consist of the actual colonies of this organism, and can have no connection with the mimosa, since at the time no mimosa had ever been brought into this tannery, which used only oak and quebracho. Similar stains were produced by inoculating damp pieces of leather with the organism.

Source of Mycoderma Tannica.—Bacteriological examination of the tan-liquors showed the presence of the following yeasts and moulds beside *M. tannica*: *Mucor mucedo, Aspergillus niger, Penicillium glaucum, Saccharomyces apiculatus, S. Pastorianus,* several *Torulas*. The number of *M. tannica* in 1 cc. of liquor varied from 60,000 to 150,000. The water used in the tannery was free from *M. tannica.* Petri dishes exposed in the air of the tanyard were found inoculated with many kinds of moulds and yeasts, including *M. tannica.* The numbers were much larger in the warm and damp months than in the winter. The air of other rooms of the tannery was almost entirely free from *M. tannica.* The author suggests that it may have come on the tan-bark or in the tanning extract.

THE ANALYSIS OF SULPHONATED OILS—REPORT OF 1919 COMMITTEE.

By G. W. Schultz, Chairman.

The work of the Committee for this year was confined to the Hart method of sulphonated oil analysis and its modifications.[1] Since this method is volumetric and involves the use of indicators whose color changes are rendered more or less obscure in an oil-water emulsion, the primary object of the Committee work was to see if concordance of results could be obtained from a number of operators. The secondary object was to compare the results obtained by the volumetric with those obtained by using the provisional methods of the Association with certain improvements recommended by the Committee of 1917.

The samples distributed among the members of the Committee consisted of: Sample No. 1—a commercial sulphonated cod oil, and Sample No. 2—consisting of 75 per cent. of No. 1, 5 per cent. of mineral oil and 20 per cent. of pressed menhaden oil. The menhaden oil contained: unsaponifiable 0.40 per cent., neutral fat 94.93 per cent., and had an acid value of 10.1 and saponification value of 191.5.

The instructions sent to the members of the Committee were as follows:

Method A.

Total Alkali.—Ten grams of the sample accurately weighed into a 250 cc. Erlenmeyer flask, dissolve in 150 cc. water (heat if necessary for complete solution) and titrate to acid end point with N/2 H_2SO_4 using 5 cc. of methyl orange as indicator. Calculate results to milligrams KOH per gram = (A).

Alkali Minus NH_3, Combined and Free Fatty Acids.—About 8 grams of the sample weighed into a 500 cc. beaker, 50 cc. of 95 per cent. alcohol added, and N/2 NaOH run in to end point with phenolphthalein; boil gently until no more NH_3 is given off (to be tested for with moist red litmus paper), cool, add N/2 NaOH again to end point and boil again to drive off any more NH_3 and repeat again if necessary. Finally cool and make alkaline to phenolphthalein with N/2 NaOH. Add 150 cc. water and 5 cc. methyl orange and titrate to acid end point with N/2 H_2SO_4.

[1] This Journal, 12, 550 (1917), and 13, 190 (1918).

The number of cubic centimeters of $N/2\ H_2SO_4$ required corresponds to the combined and free fatty acids—calculate to milligrams KOH per gram = (B). And the number of cubic centimeters of $N/2\ H_2SO_4$ minus total number of cubic centimeters $N/2$ NaOH used = alkali minus NH_3 (in the case of the presence of ammonium salts this may be a minus quantity). Calculate the number of cubic centimeters difference to milligrams KOH per gram = (C).

Saponification Value, Unsaponifiable.—About 20 grams of the sample is weighed into an Erlenmeyer flask (250 cc. capacity) and saponified with 80 cc. of N/1 alcoholic KOH (or 40 cc. of 2N solution) by boiling for 1 hour under reflux. Finally boil without a cover until all NH_3 is evolved and replace the loss of alcohol. Titrate the excess of KOH with $N/2\ H_2SO_4$ using phenolphthalein and calculate the amount of KOH used to saponify to milligrams KOH per gram = (D). Make the soap solution strongly alkaline again and add sufficient water or alcohol, as the case may be, to give a 50 per cent. alcoholic solution and boil for a few minutes under a reflux. Cool, transfer to a separatory, washing the flask with successive portions of 50 per cent. alcohol and finally with petroleum ether. Extract soap solution at least three times with petroleum ether. The petroleum ether is then washed thoroughly—first with slightly alkaline 50 per cent. alcoholic solution and finally with distilled water (and the washings are to be extracted in turn as usual). The petroleum ether extracts are then poured into a tared beaker, evaporated and dried to constant weight.

Saponification Value of Mixed Fatty Acids.—The extracted soap solution from the preceding determination is boiled to dryness in an evaporating dish, stirring constantly to avoid scorching. The dried soap is dissolved in boiling water and boiled until free from alcohol. Precipitate the fatty acids with dilute acid, transfer to a separatory and extract with ether (ethyl). Wash the ether extract with concentrated Na_2SO_4 solution until free from mineral acidity. Distill off ether, evaporate to dryness in hot air oven, filter through hot water funnel and collect about 3 grams in a tared Erlenmeyer. Weigh accurately and saponify with 20 cc. of N/1 alcoholic KOH by boiling for 15 minutes under

reflux. Titrate excess of KOH with N/2 H_2SO_4 and calculate the saponification value (milligrams KOH/gram) = (E).

Combined SO_3.—Eight grams of the sample weighed into a 300 cc. Erlenmeyer and boiled for 1 hour with 25 cc. of N/2 H_2SO_4 under a reflux condenser. Shake frequently. The condenser is washed out into the flask with distilled water. To the cooled mixture add about 20 cc. of ether (or enough to dissolve the fat), 100 cc. of distilled water, 25 cc. of concentrated salt solution and 5 cc. of methyl orange indicator and titrate with N/2 NaOH to alkaline end point, stopper the flask and shake well to remove any acid that may be occluded in the oil layer. The addition of ether and salt solution will facilitate the titration and make the end point easier to observe. The number of cubic centimeters of N/2 NaOH minus number of cubic centimeters N/2 H_2SO_4 added = H_2SO_4 liberated, calculate to milligrams KOH per gram = (F).

Results:

$$*NH_3 = \frac{(A - C)17.03 \times 100}{56.1}.$$

$$\text{Total fat} = \frac{(D + C) \times 100}{E}.$$

$$\text{Neutral fat} = \frac{(D + C) - B \times 100}{E}.$$

$$*\text{Combined } SO_3 = \frac{(F + A)\,80 \times 100}{56.1}.$$

Method B.

Unsaponifiable.—Weigh approximately 10 grams of oil into an 8-ounce Erlenmeyer flask and add 5 cc. aqueous KOH solution (50 grams KOH in water and dilute to 100 cc.), 45 cc. ethyl alcohol and a few glass beads. Boil 1 hour with reflux condenser. Add 40 cc. water and cool. Transfer to separatory funnel and shake at least three times with petrolic ether (boiling point 40° to 75° C.) using 50 cc. each time. Wash ether layer at least three times, first washing to be with slightly alkaline 50 per cent. alcohol and subsequently with distilled water. Evaporate ether extract in tared vessel, cool and weigh.

* In these calculations the milligrams are used as decimal fractions of a gram.

Note: If the contents of the flask bump violently during saponification, add 25 cc. petrolic ether, and proceed.

Total SO_3.—Weigh approximately 4 grams into an Erlenmeyer flask and boil for 40 minutes with 30 cc. HCl (1 : 15). Shake frequently. Cool, transfer to separatory funnel and shake out with sulphuric ether. Draw off aqueous layer and wash ethereal layer three times with 75 cc. of water, using some dilute HCl if necessary to break emulsion. Combine washings with main aqueous portion and the sulphuric acid determine as barium sulphate. From the amount thus found, the quantity as determined below is subtracted and the difference calculated as SO_3.

SO_3 as Salts.—Dissolve 8 grams in ether and shake out several times with 25 cc. concentrated brine free from sulphates. Combine the washings, dilute, acidify with HCl, filter and determine the sulphuric acid as barium sulphate.

Total Fatty Matter.—Place the ether solution from total SO_3 determination in tared dish or flask, evaporate or distill off ether and dry, cool and weigh residue.

Ammonia.—Extract 10 grams of the oil dissolved in 150 cc. sulphuric ether in a separatory funnel four times with 10 cc. dilute H_2SO_4 (1 : 15). Determine ammonia by distillation as in the Kjeldahl method.

Neutral Oil.—Weigh about 10.0 grams in Erlenmeyer flask, add 50 cc. alcohol, boil reflux 5 minutes and titrate with normal NaOH till permanent pink, using phenolphthalein as indicator. Then wash into separatory funnel and extract unaltered oil with petrolic ether as in non-saponifiable.

The results tabulated were received from the following members of the Committee:

Messrs. Faust & Fortner, Yocum Faust Laboratory, London, Ontario, Canada.

L. J. Vaudreuil, Graton & Knight Manufacturing Co. Laboratory, Worcester, Mass.

John H. Yocum & A. G. Lloyd, Newark, N. J.

R. Boehringer, National Oil Products Co., Harrison, N. J

Dr. G. Bumcke, F. S. Walton Co., Philadelphia, Pa.

G. W. Schultz, Elk Tanning Co. Laboratory, Ridgway, Pa.

TABLE I.—Sample No. 1, Method A.

		Faust and Fortner Per cent.	Vaudreuil Per cent.	Yocum and Lloyd Per cent.	Boehringer Per cent.	Bumcke Per cent.	Schultz Per cent.	Greatest difference Per cent.	Average analysis Per cent.
Ammonia	1	0.14	0.15	0.14	0.22	0.19	0.18	0.09	0.17
	2	—	0.13	—	0.23	0.23	0.18		
Unsaponifiable	1	0.32	0.49	—	0.60	0.43	0.49	0.24	0.46
	2	—	—	—	0.52	0.42	0.48		
Total fatty matter	1	79.00	—	—	65.80	70.96	69.82	13.15	71.25
	2	—	—	—	65.90	70.13	69.31		
Neutral fat	1	31.20	—	—	26.60	29.79	30.21	4.45	29.35
	2	—	—	—	26.90	29.24	29.60		
Combined SO_3	1	4.81	3.85	4.35	4.51	4.33	4.05	0.94	4.30
	2	—	3.89	—	4.45	4.15	4.03		

Sample No. 1, Method B.

		Faust and Fortner Per cent.	Vaudreuil Per cent.	Yocum and Lloyd Per cent.	Boehringer Per cent.	Bumcke Per cent.	Schultz Per cent.	Greatest difference Per cent.	Average analysis Per cent.
Ammonia	1	0.14	0.19	0.16	0.24	0.24	0.19	0.10	0.19
	2	—	—	—	—	0.20	0.19		
Unsaponifiable	1	0.37	0.47	0.55	0.55	0.39	0.47	0.18	0.48
	2	—	—	—	—	0.44	0.53		
Total fatty matter	1	69.15	72.06	69.93	70.60	70.99	70.73	2.91	70.52
	2	—	—	—	—	70.57	70.50		
Neutral fat	1	19.26	—	17.08	17.40	18.33	17.68	2.18	17.96
	2	—	—	—	—	18.28	18.80		
Combined SO_3	1	3.50	4.40	4.13	4.56	4.47	4.34	1.06	4.25
	2	—	—	—	—	4.35	4.59		
Total SO_3	1	4.78	4.65	4.79	5.04	4.97	4.97	0.39	4.86
	2	—	—	—	—	4.95	5.00		
SO_3 as salts	1	1.28	0.25	0.66	0.48	0.50	0.63	1.03	0.62
	2	—	—	—	—	0.60	0.41		

TABLE II.—SAMPLE NO. 2, METHOD A.

		Faust and Fortner Per cent.	Vaudreuil Per cent.	Yocum and Lloyd Per cent.	Boehringer Per cent.	Bumcke Per cent.	Schultz Per cent.	Greatest Difference Per cent.	Average analysis Per cent.
Ammonia	1	0.10	0.09	0.12	0.17	0.20	0.11	0.09	0.14
	2	—	0.09	—	0.16	0.15	0.12		
Unsaponifiable . . .	1	4.72	—	—	5.40	5.51	5.38	0.71	5.24
	2	—	—	—	5.33	5.34	5.49		
Total fatty matter . .	1	81.45	—	—	68.80	73.60	71.45	12.30	73.67
	2	—	—	—	69.50	71.45	71.62		
Neutral Fat	1	47.03	—	—	38.00	41.76	40.52	8.68	41.64
	2	—	—	—	38.70	39.12	40.94		
Combined SO_3	1	3.69	2.99	3.62	3.32	3.60	3.18	0.67	3.38
	2	—	3.05	—	3.39	3.23	3.13		

SAMPLE NO. 2, METHOD B.

		Faust and Fortner Per cent.	Vaudreuil Per cent.	Yocum and Lloyd Per cent.	Boehringer Per cent.	Bumcke Per cent.	Schultz Per cent.	Greatest difference Per cent.	Average analysis Per cent.
Ammonia	1	0.15	0.15	0.14	0.15	0.16	0.14	0.02	0.15
	2	—	—	—	—	0.14	0.14		
Unsaponifiable	1	5.55	5.54	5.79	5.37	5.46	5.64	0.42	5.54
	2	—	—	—	—	5.36	5.46		
Total fatty matter . .	1	71.65	70.56	71.89	71.93	72.68	72.16	2.16	71.83
	2	—	—	—	—	72.75	72.25		
Neutral fat	1	31.35	—	31.32	32.03	31.98	31.74	1.44	31.81
	2	—	—	—	—	33.54	31.41		
Combined SO_3	1	2.50	3.32	2.90	3.40	3.36	3.29	0.90	3.12
	2	—	—	—	—	3.27	3.36		
Total SO_3	1	3.50	3.60	3.46	3.75	3.73	3.73	0.29	3.63
	2	—	—	—	—	3.71	3.75		
SO_3 as salts	1	1.05	0.28	0.56	0.35	0.37	0.44	0.77	0.51
	2	—	—	—	—	0.44	0.39		

TABLE III.—METHOD A.

	Sample No. 1 Average of three analyses Per cent.	Sample No. 2 Calculated from average of No. 1 Per cent.	Sample No. 2 Average of three analyses Per cent.	Difference Per cent.
Ammonia	0 21	0.16	0.16	0.00
Unsaponifiable	0 49	5.45	5.41	0.04
Total fatty matter	68.69	71.52	71.24	0.28
Neutral fat	28.73	40.54	39 84	0.70
Combined SO_3	4.25	3 19	3.31	0.12

METHOD B.

	Sample No. 1 Average of three analyses Per cent.	Sample No. 2 Calculated from average of No. 1 Per cent.	Sample No. 2 Average of three analyses Per cent.	Difference Per cent.
Ammonia	0.23	0.17	0.15	0.02
Unsaponifiable	0.49	5.45	5.44	0.01
Total fatty matter	70.67	73.00	72.29	0.71
Neutral fat	17.98	32.47	32.13	0.34
Combined SO_3	4.45	3.34	3.35	0.01
Total SO_3	5.00	3.75	3.74	0.01
SO_3 as salts	0.55	0.41	0.39	0.02

TABLE IV.—RESULTS OBTAINED UNDER METHOD A FROM WHICH THE CALCULATIONS WERE MADE. SAMPLE NO. 1.

		Faust and Fortner Mmg. KOH/gram	Vaudreuil Mmg. KOH/gram	Yocum and Lloyd Mmg. KOH/gram	Boehringer Mmg. KOH/gram	Bumcke Mmg. KOH/gram	Schultz Mmg. KOH/gram
Total alkali	1	5.05	0.55	5.32	5.32	5.91	5.07
	2	—	0.54	—	5.22	5.71	5.14
Alkali—NH_3	1	0.40	−4.48	0.70	−1.96	−0.49	−0.73
	2	—	−3.94	—	−2.24	−1.77	−0.78
Combined and free fatty acids	1	76.03	74.66	79.80	79.60	78.16	77.81
	2	—	73.90	—	79.00	77.62	77.89
Sap. val. of sample	1	141.8	132.9	133.96	135.5	135.2	137.8
	2	—	134.3	—	135.7	134.9	136.6
Sap. val. of mixed fatty acids	1	180.0	—	—	202.7	189.8	196.4
	2	—	—	—	202.5	189.8	196.0
Combined SO_3	1	28.70	26.45	25.20	26.31	24.47	23.30
	2	—	26.77	—	25.99	23.36	23.09

SAMPLE NO. 2.

		Faust and Fortner Mmg. KOH/gram	Vaudreuil Mmg. KOH/gram	Yocum and Lloyd Mmg. KOH/gram	Boehringer Mmg. KOH/gram	Bumcke Mmg. KOH/gram	Schultz Mmg. KOH/gram
Total alkali	1	3.92	0.38	4.76	3.84	3.94	3.50
	2	—	0.39	—	3.81	4.14	3.67
Alkali—NH_3	1	0.8	−2.61	0.70	−1.72	−0.83	0.00
	2	—	−2.41	—	−1.34	−0.92	−0.28
Combined and free fatty acids	1	58.20	58.69	62.65	61.35	61.27	61.06
	2	—	58.40	—	61.45	61.66	60.48
Sap. val. of sample	1	139.3	134.7	134.7	139.1	142.40	141.1
	2	—	138.5	—	140.8	137.2	141.4
Sap. val. of mixed fatty acids	1	172.0	—	—	200.0	192.3	197.4
	2	—	—	—	200.0	190.7	197.0
Combined SO_3	1	22.0	20.56	20.65	19.44	21.31	18.80
	2	—	20.98	—	19.96	18.48	18.30

COMMENTS.

FAUST AND FORTNER: As regards total fatty matter, we believe method B to give more reliable results in the average chemist's hands than method A, although we believe the present provisional methods sufficiently accurate for commercial purposes.

Method A, for combined SO_3 seems a good method to operate, but gives results very much higher than method B. If this method gives concordant results by the members of the Committee, we would be in favor of it as against method B, which is the same as our present provisional method.

The question of neutral oil remains to be solved, in that, method A gives considerably higher results than method B, a fact which has been brought out before, and we have no way of telling which method is the more correct.

Our experience with method A has not been very satisfactory; we found it necessary to re-standardize the caustic potash solution every day, and a small error in any one of the determinations affects the entire analysis. The only two suggestions that we would make are dependent on concordance of results obtained by the Committee; these two suggestions being, to substitute the procedure for combined SO_3, as given in method A, in place of the present provisional method; and the second suggestion being, to include in the present provisional methods the procedure given for neutral oil in method B.

DR. G. BUMCKE: The titration of solutions or emulsions of sulphonated oils with methyl orange as indicator makes the determination of the end point more or less difficult on account of their own color and, therefore, gives somewhat uncertain results.

In the determination of alkali minus NH_3 and combined and free fatty acids, the boiling with a little excess of lye to drive off the NH_3 may start saponification and thus influence the result.

For the determination of the saponification value of the original sample and the unsaponifiable, the use of 20 grams oil and 80 cc. N alcoholic KOH is unnecessary as this does not give better results than the use of 2-3 grams and 25 cc. N/2 KOH for determining the saponification value, and 8-10 grams for determining the unsaponifiable. The two tests made with these smaller quantities can be made much quicker than when working with the larger quantity, especially is the extraction with

petrolic ether very tedious, difficult and slow on account of the formation of a thick, white, gelatinous, middle layer.

	Sample No. 1	Sample No. 2
Sap. value (using 2-3 grams	136.3 / 137.2 } 136.8	139.4 / 138.7 } 139.1

Four years ago I suggested the use of the total fatty matter for the determination of the unsaponifiable, but the removal of the disturbing sulpho-compounds might be done in one operation, namely, by boiling 8-10 grams of oil with 25-30 cc. of diluted HCl for 30-45 minutes, then adding 75-100 cc. alcohol and sufficient KOH and boil again for 1 hour. The extraction with petrolic ether will not cause quite as many difficulties as in the former procedure. The amount of unsaponifiable found will even be a little larger as some of the compounds that help to form the gelatinous middle layer are broken up and cannot retain any of the unsaponifiable as seems to be the case in the other method.

Boiling first with acid, then with alcoholic lye and extracting four times with petrolic ether, the amount of unsaponifiable was found to be:

Sample No. 1	Sample No. 2
0.74 / 0.66 } 0.70 per cent.	5.86 / 5.88 } 5.87 per cent.

while by the method given

0.42 per cent. and 5.42 per cent.

was found.

Another advantage of this method is that the fatty acids, which are obtained from the soap solution after driving off the alcohol and acidifying with HCl are free from sulpho-fatty acids and are almost entirely soluble in ether; while the soap from the process as given in method A contains all of the sulpho-fatty acids which are only partly soluble in the ether solution of the fatty acids. The larger part of these sulpho-acids settle on the bottom of the flask. The part which went into the ether solution will, after the ether is driven off, decompose when the fatty acids are dried and the free sulphuric acid will char them. This cannot happen when the sulpho-acids are eliminated.

When obtained in the manner suggested only the fatty acids of the second oil showed a slight deviation in the saponification value:

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Sample No. 1		Sample No. 2	
190.1 189.7	189.9 per cent.	193.1 193.6	193.4 per cent.

In order to investigate the right amount of neutral oil, which differs considerably in methods A and B, I applied the method described, this JOURNAL, 10, page 564 (sulphuric ether extraction) and found:

Sample No. 1		Sample No. 2	
23.52 23.61	23.57 per cent.	41.89 41.80	41.85 per cent.

As these figures do not prove anything and do not agree with those of either method A or B, the complete analysis of both oils was made in order to find the amount of neutral oil by difference. The following results were obtained:

	Sample No. 1		Sample No. 2	
Water (heated in silica crucible on steam plate).........	20.16 20.25	20.21 %	15.15 15.15	15.15 %
Total fatty matter (method B).	70.78			78.13
Total SO_3 (method B)	4.958			3.717
NH_3 (method B)	0.220			0.148
Na_2O	2.232 2.226	2.229	1.679 1.681	1.680
Glycerine and loss (by diff'rce)	1.603		1.175	
	100.000		100.000	
SO_3 in salts..................	0.546		0.403	
Combined SO_3.....	4.412		3.314	
Sulpho fatty acids	20.95		15.74	
Acid value	77.59 76.30	76.95	61.13 60.96	61.05

Sample No. 1		Sample No. 2	
0.22 NH_3	0.401 Na_2O	0.148 NH_3......	0.270
Amount of alkali found	2.229 Na_2O		1.680
Total amount as Na_2O.	2.630		1.950
0.546 SO_3 (in salts) combine with	0.432 Na_2O	0.403 SO_3 (in salts)	0.312 Na_2O
4.412 combined SO_3 combine with	1.710 Na_2O	3.314 com. SO_3	1.284 Na_2O
	2.142 Na_2O		1.596 Na_2O
4.65 fatty acids combine with..........	0.488 Na_2O	3 31 fatty acids..	0.354
Total Na_2O......	2.630		1.950
Acid value 76.95	40.52 fatty acids	61.05........ ...	31.56 fatty acids
Combined with Na_2O.	4.65 fatty acids		3.31 fatty acids
Total fatty acids.	45.17 per cent.		34.87 per cent.
Total fatty matter	70.78 per cent.		78.13 per cent.
Neutral oil..........	25.61 per cent.		43.26 per cent.

The nearest to these figures for neutral oil are those obtained by the sulphuric ether extraction method, and for this reason this method should have the preference against the others; especially the petrolic ether extraction, as it seems not able to dissolve as much of the neutral compounds as ether.

In the determination for neutral oil under method B, the oil should not be titrated hot, as saponification will begin.

The wide variation between the different members of the Committee is shown in Tables I and II. In Table III is given the average analyses of samples No. 1 and No. 2 for both methods of analysis. These results are compiled from those of the three members of the Committee in closest agreement. This shows that as far as sample No. 2 is concerned, it is possible to obtain that which was introduced by either method. But this proves nothing as it is not known which method gives the correct analysis of sample No. 1. Table IV is given to show the wide variation in most of the results obtained by method A.

The Chairman is of the opinion that, with more familiarity with the end point changes, in method A, the different members of the Committee would be able to obtain results that would agree very well with one another. Nevertheless, he thinks that the gravimetric method would give more reliable results with the average analyst and it alone should be considered for the official method of the Association. However, it is to be recommended that much more work should be done on it, paying particular attention to the details of each determination separately. Tables I and II show that the determination for "SO_3 as salts" under method B gives the highest percentage of variation in the results recorded. This determination demands the most urgent study; as it is responsible for the unreliable results under combined SO_3, providing that the determination for total SO_3 is accurate.

The determination of neutral fat needs further investigations and Dr. Bumcke has given a valuable suggestion for further work.

The total fat determination should receive further attention, as it is questionable whether the results obtained in this determination give the true value, although the results of the majority of the Committee, under method B, check very well.

The Chairman, in the absence of comments from the majority of the Committee, can only recommend that future work of the Committees for Analysis of Sulphonated Oils be confined to perfecting the method as outlined in method B for an official method of the Association.

COLLOID CHEMISTRY OF TANNING.*

By Professor H. R. Procter, University of Leeds.

General Review.**

The conversion of skin into leather is an art dating back many thousand years, and the group of phenomena now classed as capillary or colloid has also been long known, though the relation of the two is a matter of modern knowledge. Under these circumstances it is difficult to know where to begin the discussion, and the question is further complicated by the work of the present writer and his pupils, who have recently shown that much which has been attributed to the surface-action which is implied in the name "capillary chemistry" is really subject to more general laws, and can be fully explained by mass action, electro-chemical attraction, and osmotic pressure. The title must, therefore, be taken, with a wider meaning than its etymology would imply, to include much of physical chemistry, complicated, however, by structure and the special properties of colloids.

The skin is constituted of collagen (probably a polymerized anhydride of gelatine) and physically is a network of fibers of colloidal jelly. In its natural state it has an outer coat of epidermis, with its hair and sebaceous and sudoriferous glands, but it is not necessary in this report to consider in detail the chemical, mechanical, and bacteriological processes which are used to free it from these appendages or to separate its fiber-bundles into their smaller constituent fibers. These gelatinous fibers in the dried raw hide adhere together to form an almost homogeneous horny mass, and the problem of the tanner is so to treat them, either by chemical change or by surface-coating, as to prevent their adhesion, so that on drying they remain isolated and free

* British Association for the Advancement of Science. First Report on Colloid Chemistry and its Industrial Applications, 1917.

** Among the abbreviations employed in this section are the following. *Coll.* = *Collegium;* J. A. L. C. A. = Journal of the American Leather Chemists Association; *L. Coll.* = *London Collegium*, Jan., 1915, to June, 1917; *T. C. S.* = Transactions of Chemical Society (London).

to move, and the skin consequently flexible and porous, and at the same time without tendency to putrefactive change. While the durability of wet raw hide is measured in days or weeks, Roman boots have been dug up which are hardly in worse condition than those which the tramp leaves, worn out, at the roadside. The methods employed by the tanner, though very similar in their effects, are so various that no single explanation, physical or chemical, will cover all of them; and often various actions are combined to produce the desired result.

The first general problem, then, regards the nature of the jelly state, which has many peculiarities. Van Bemmelen[1] and Bütschli[2] believed it to be a network or cellular structure of microscopic dimensions, and this view long held the field, but is now abandoned for that which regards it as a solid or semi-solid solution of which the colloid and water (or some other solvent) are the constituents. The question is still an open one whether the colloid is in the form of "micellae" (submicroscopic particles) or of large conjugated or polymerized molecules, but this is mainly a matter of terms, and at least it is clear that the mixture is so intimate that both constituents are within the range of molecular and electro-chemical forces.

The colloid most fully investigated in this relation is gelatine, which in its chemical constitution is almost identical with hide fiber, while its homogeneous character renders exact quantitative study much more possible. Soaked in water at laboratory temperatures, it does not dissolve, but swells to a definite volume dependent to some extent on the particular sample and the temperature. When the temperature is raised above 25° the jelly melts and becomes miscible in water in all proportions, though even when diluted considerably beyond its original equilibrium volume, it still "sets" on cooling to a coherent elastic mass. Gelatine, both as jelly and solution, always shows a slight Tyndall effect, reflecting a beam of light sideways; but the ultramicroscope shows no defined particles. Arisz[3] has shown that the Tyndall effect increases with concentration and with lowered tem-

[1] *Z. Anorg. Chem.*, 1896, 13, 304; 18, 15.

[2] Untersuchungen über mikroskopische Schaume und das Protoplasma, Leipzig, 1892. Verh. des naturh.-med. Vereins zu Heidelberg, 1892, N. F. 5, 28-41; *ibid.*, 42-43; *ibid.*, 1893, 89-102; *ibid.*, 1896, 457-472; *ibid.*, 1894, 230-292.

[3] *Kolloidchem.*, Beihefte, 1915, 7, 22.

perature, but without any break or sudden change at the setting point. The viscosity shows a similar increase, with no actual break, but a rapid rise at the temperature of gelatinization, below which it speedily becomes too great to measure by ordinary methods. Both these effects are reversed on gradual heating, but there is a "lag" in both directions, a cooling solution only acquiring its full viscosity and Tyndall effect after the lapse of considerable time, which may even extend to weeks, but below 60°, given time, the process seems completely reversible. Above 60°-70° some permanent change takes place (hydrolysis or depolymerization) which results in lowered viscosity, Tyndall effect, and setting power. These facts are best explained by the hypothesis that below 60° the gelatine solution is one of molecules or small molecular aggregates, which, as temperature falls, gradually unite to form larger ones, and at the setting point unite to a complete molecular network analogous to a mass of tenuous crystals. Cases are known in which such crystalline masses closely simulate colloid jellies. Time is of course needed for this rearrangement, as it is for actual crystallization, and owing to the size and comparative immobility of the particles, rearrangement is very slow. Kundt[4] has shown that under the influence of rapid flow at 18° (which is below the setting point) even very dilute and quite liquid solutions of gelatine show the polarization effects of strain, while no such effect could be observed with glycerine or sugar solutions of much higher viscosity. The writer proposes to repeat these experiments at higher temperatures, but in the meantime it is clear that the viscosity of such solutions is not due simply to liquid friction, but includes an element of strain.

Proteids, among which gelatine must be included, are now known to consist of open or closed chains of amino-acids linked by the carboxyl group of one to the amino group of the next with elimination of OH_2. In closed chains, groups within a single molecule, forming terminal amino and carboxyl groups are also similarly united ring-structures. In this case the molecule is electrically neutral, and non-reactive till the ring is broken, while the open chains are amphoteric—basic by their terminal amino-group and acid by their carboxyl. A very useful practical

[4] *Wied Ann.*, 1881, 13, 110.

distinction is that ring proteids are unattacked by trypsin alone, while pepsin is able to open the ring.[5] Gelatine can be digested by trypsin, but collagen is only attacked by pepsin, hence the view, supported by other facts, that collagen is the ring or anhydride form of gelatine into which it is converted by continued boiling or by the action of acids or alkalies.

If gelatine (or hide fiber) be placed in dilute acid, it swells very much more than in water alone, and at the same time a considerable amount of free acid disappears (*i. e.*, is no longer capable of reddening methyl orange). The effect is most readily investigated with a strong monobasic acid such as hydrochloric acid. In this case the maximum swelling, which may reach an absorption of 50 cc. of liquid for 1 gram of dry gelatine, occurs at an acid concentration under 0.005 N, from which it rapidly falls in a curve of hyperbolic type as the concentration is increased, the equilibrium being completely reversible up to about 0.25 N, beyond which some secondary reaction, probably a further breaking up of the proteid chain begins to take place. At the same time the total absorption of acid steadily increases with concentration in a curve which may be closely represented by the ordinary adsorption formula, $a = kx\frac{1}{p}$ (where a is total acid, x the concentration of external solution, and k and p are constants); but which is really due to a complicated osmotic equilibrium which must be further explained.[6]

Gelatine, being amphoteric, acts as a very weak alkali in presence of hydrochloric acid, and forms a gelatine chloride, which like most salts is highly ionized (in fact to practically the same extent as hydrochloric acid itself). The base, however, is very weak, its ionization being of the same order as that of water,

[5] Plimmer, "Chemical Constitution of the Proteids," Part II, p. 11 (Sec. ed., Longmans, Green & Co.). The statement seems to require confirmation.

[6] It may be well to point out here that the "adsorption formula" just quoted is absolutely void of theoretical basis, as regards adsorption, but is a mathematical expression which will closely represent any chemical or physical phenomenon which proceeds at a diminishing ratio. It is, for instance, the exact law of distribution of a solute between two immiscible solvents, in one of which its molecular complexity is p times that in the other.

and consequently the salt is largely hydrolyzed, and can only exist in the presence of free acid. Thus gelatine base, gelatine chloride, and free hydrochloric acid are necessarily present in such a jelly in proportions determined by the concentration of the acid, and instead of a definite point of neutrality such as is given by a strong base, we have only a curve approaching, but never reaching, complete neutralization. This is the explanation of the apparent indefiniteness of proteid compounds, which has led many chemists to deny the existence of definite proteid salts. By determining the hydrolysis curve and calculating the upper limit to which it tends, it is possible to calculate quite definite combining equivalents. Procter[7] in this way, on the assumption that gelatine had a second valency negligible at low acid concentrations, found a combining weight of 839, while Wilson,[8] from the same experiments, but regarding the apparent second valency as due to incipient decomposition or experimental error, found 768. It is not to be supposed, however, that these comparatively low weights represent the real complexity of the probably polymerized molecule in aqueous solution, but merely the smallest molecular division chemically possible.

It has been stated that the swelling of gelatine in acids is due to a complicated osmotic equilibrium, and that it reaches a maximum at a very small acid concentration, and is repressed if the concentration is increased. A similar repression is caused by the addition of any salt with the same anion to the outer solution, and as neutral salts have no decomposing effect on gelatine, the repression can be carried much further than with acid; thus a chloride jelly treated with sodium or potassium chloride is reduced to a horny mass. Seeing that the jelly is almost as permeable as water both to ionized and unionized salts and acids, it is hard to see how this repressive osmotic pressure is exerted. The following is the explanation.

In equilibrium between a jelly and its external solution not only must all osmotic pressures be equally balanced, but, as has been shown by Donnan,[9] the electro-chemical condition must be fulfilled that the products of the concentrations of any pair of

[7] *T. Chem. Soc.*, 1914, 105, 320.

[8] J. A. L. C. A., 1917, 12, 108.

[9] *Zeits. Elektrochem.*, 1911, 17, 572; Donnan and Harris, *T. Chem. Soc.*, 1911, 99, 1575.

diffusible anions and cations common to both phases must be equal. Thus with gelatine chloride and free acid the chloridions multiplied by the hydrions must be equal in the jelly and the external acid. On the other hand, the osmotic pressures depend not on the products, but simply on the sum of diffusible particles present. In the external acid the numbers of hydrions and chloridions are obviously equal, while in the jelly the chloridion of the gelatine chloride is added to the equal hydrion and chloridion concentrations of the free acid present, thus making the final concentrations of these ions in the jelly unequal. Now, as the sum of two unequal factors is always greater than that of two equals giving the same product, or, geometrically the perimeter of a square is always less than that of any other rectangle of equal area, and as the sides represent the osmotic pressure, while the area represents the product, it is clear that the two equalities cannot at once be completely fulfilled, but in electrochemical equilibrium the osmotic pressure must be in excess and the jelly must tend to swell unlimitedly and finally to dissolve. That it does not do so is a consequence of its colloid nature, which depends on cohesive attractions drawing the colloid particles together to polymerized masses or to a continuous network, and which consequently opposes swelling and solution, while the diffusible ions are held to the colloid ions by electro-chemical attractions, and, as they cannot escape from the jelly, tend to drag it apart and dilute it by absorption of the external acid, from which they expel a part of its acid concentration. The equilibrium is, therefore, a very complex one, but finally depends on the excess of internal osmotic pressure being balanced against the internal attraction or cohesion of the colloid particles, both ions and molecules. For its mathematical discussion the reader must be referred to original papers by Procter and his pupils. It will, however, be obvious that as the external solution becomes more concentrated the proportion of absorbed acid (or salt) is increased, while that of gelatine chloride is limited to the quantity of gelatine present. The difference of concentration of hydrion and chloridion in the jelly is therefore diminished, and it contracts under the influence of its own internal attractions. Precisely similar considerations apply to the action of alkalies on gelatine. Ionizable salts are formed by combination of the

base with the carboxyl group of the proteid, and the osmotic equilibrium is with the cation and OH instead of with the anion and H. Neutral gelatine, as an amphoteric body, of course, ionizes to a limited extent with water alone, and its dissociation constants are of the same order of quantity as those of the water with which it is in equilibrium. It is, however, slightly stronger as a base than as an acid, and consequently its neutral point of minimum swelling is slightly on the alkaline side. This has important bearings on manufacturing practice, the greatest flaccidity of the raw skin, which is required for the softest leather, being obtained in weakly alkaline liquids.

It has been pointed out by Donnan[10] that in consequence of the unequal distribution of positive and negative diffusible ions which has just been described, the surface of an acid or alkaline jelly in equilibrium has necessarily an electrical charge or potential, greatest at the maximum swelling, and such charges seem an essential condition of the colloid state. The surface is positive or negative according to whether the diffusible anion or cation is retained in the colloid. Thus gelatine and hide fiber are negative in alkaline and positive in acid solutions, and it will be shown later that this has an important bearing on the theory of leather manufacture.[11]

Wilson[12] has extended these facts to a general theory of colloids and adsorption, showing that all surfaces must possess a potential due to unbalanced chemical forces on the surface, and, therefore, in a liquid containing electrolytes must condense ions or particles of the one sign on its surface, and repel those of the opposite sign; and also showing that surfaces must, therefore, be surrounded with a film of liquid of different concentration to the bulk, to which the same considerations and equations are applicable as to the absorbed solution of colloid jellies. For fuller mathematical treatment the reader is referred to original papers.

Some of the views just explained are so recent that their bearing on actual tanning processes has hardly had time to make itself felt in technical literature, and for its latest applications papers

[10] *Zeits. Elektrochem.*, 1911, 17, 579.

[11] See below and papers under 13.

[12] *Jour. Am. Chem. Soc.*, 1916, 38, 1982.

by Procter and Wilson must be consulted,[13] but a brief summary may here be given.

As has been explained, the leather-hide, freed from epidermis, consists of a sort of felt of fibers of gelatigenous tissue, which are themselves bundles of finer fibrils cemented together by some substance nearly identical with, but somewhat more soluble than that of the fibrils themselves. Treated with dilute alkalies or acids, this cementing substance is more or less completely dissolved, and the fibrils themselves are swollen. Accurate chemical investigation of skin is complicated by this fact of structure, for while the free acid or alkali absorbed in the jelly of the fiber is subject to the mathematical laws which have been explained, the interstices between the fibers are also filled with external solution by capillarity, and no accurate means has been found of measuring the proportion between the two. Hide swollen in acid or alkali is tense and firm, and containing its liquid in jelly-form in the fibers only parts with it under heavy pressure; but when the fibers are dehydrated by neutralization, the skin becomes "fallen" or flaccid, and apparently much wetter, since the imbibed water is easily squeezed out. If in this condition the loose water is removed by soaking in alcohol or other dehydrating agents, the fibrils no longer adhere to each other, and a soft leather is produced, which, however, on again soaking in water, rapidly returns to its raw or "pelt" condition.[14] If, however, a little stearic acid is dissolved in the alcohol so as to coat and partially waterproof the dehydrated fibrils, the leather at once becomes tolerably permanent. This led Knapp to the view that the process of tanning was merely an isolating and coating of the fibrils, and, though the explanation is incomplete, it unquestionably is part of the true one.

In order to make a soft leather, it is, therefore, necessary to have the skin in a flaccid or unswollen condition, and assuming that it has been swollen by lime, this is brought about essentially by neutralization. The older processes depend on fermentations

[13] Procter, *Koll.*, Beihefte, 1911, 2, 270; *T. Chem. Soc.*, 1914, 104, 313; and Wilson, *T. Ch. S.*, 1916, 109, 307; "Swelling of Colloid Jellies," J. A. L. C. A., 1916, 11, 399; and Burton, D., "The Swelling of Gelatinous Tissues," *J. S. C. I.*, 1916, 35, 404.

[14] Knapp, *Natur und Wesen der Gerberi*, Braunschweig, 1888; Meunier and Seyewetz, *Coll.*, 1912, 11, 54.

of bran, pigeon and dog dung, and the like, and just as liming serves the several purposes of swelling the hide, loosening the hair, and partially saponifying the fat, so these fermentation processes not merely neutralize the lime by weak acid, or salts of weak bases, but remove cementing substance from the fibers by the digestive effects of bacterial enzymes, and complete the emulsification of fats and the solution of residues of the epidermis. It is obvious that the attainment of all these varied results by an artificial preparation is no easy matter, but an approach to a complete solution has been made by J. T. Wood[15] (followed by Dr. Röhm, who has improved working details), by a mixture of ammonium chloride and pancreatic digestive ferments, which for many purposes fulfills its object better and much more safely than the old materials. The tryptic ferments dissolve the epidermis residues and cement substance, but scarcely affect the collagen fibers (v. s.). They also facilitate emulsification of fats by reducing the surface tension between jelly matters and the liquid, while the presence of free ammonia and excess ammonium salts regulates the hydroxyl concentration to something near the alkalinity required for minimum swelling (v. s.). Possible improvement lies in the direction of the discovery of new enzymes, and of suitable weak bases and "buffer" substances, to give the precise degree of solution and of acidity or alkalinity required for the various leathers. For firmer leathers the use of weak acids regulated by excess of their salts produces a sufficient degree of neutralization and flaccidity.

We must now consider the conversion of the still raw and very putrescible skin into permanent leather. We have seen that this can be accomplished by dehydrating the fibrils without allowing them to adhere (v. s.), and by coating them with water-resisting substances; but it is known that similar effects of an even more permanent character can be produced by reagents (notably formaldehyde and bromine) which act chemically on the collagen fiber, rendering it insoluble in water, but which in their nature cannot deposit any exterior coating such as was assumed by Knapp. We must, therefore, conceive the process as being in most cases a combination of both chemical and physical effects, of which sometimes one, sometimes the other, preponderates,

[15] Wood, "Puering, Bating and Drenching," Spon, 1912, p. 186.

according to the method employed. We have also to consider reactions which from their colloid character differ somewhat widely from those of free ions to which the term "chemical" is generally applied. It is, therefore, best to proceed from simple cases of which definite explanation can be given, to the complex in which more than one sort of reaction takes place.

Knapp's alcohol leather, in which a material is produced with all the physical characteristics of a complete leather by simple dehydration of the hide fibers under conditions preventing adherence, has been already mentioned (v. s.). The theory of acid swelling has also been described, and it has been shown that as the anion concentration of the external solution is increased the difference of osmotic pressure between it and the jelly which causes swelling is diminished without limit, and the fiber contracts by its internal attractions. This fact is applied in the process of "pickling" which is principally employed in the preservation of sheepskins before tanning. The skins, after unwooling, are treated in a bath of dilute acid, generally sulphuric, to which some salt is added to prevent excessive swelling, and are then transferred to a saturated solution of common salt. The dehydration of the fiber is very great—the skin becomes thin and flat and can be preserved almost unlimitedly in the wet condition; and if dried out and loosened by a little mechanical stretching, forms a very perfect white leather, which, however, softens and swells at once in water through the removal of the restraining salt. It is not essential that the acid should be a "strong" one. Skins pickled with formic acid and salt by Mr. Seymour-Jones were sent on a voyage up the Amazon, and returned in perfect condition. It is obvious that if a skin swollen with some acid other than hydrochloric be subsequently treated with salt, a quadruple equilibrium results, most of the proteid salt being converted into chloride by the great excess of sodium chloride, with the formation of the sodium salt of its acid, each proteid salt being balanced against its own anion in the external solution. In a direct experiment with gelatine formate almost the whole of the formic acid was replaced by hydrochloric. It is probable that the so-called "free" hydrochloric acid in the gastric juice has been liberated in this way, and really exists as a salt of some weak colloid base.

In the ordinary processes of production of "alumed leathers" it is impossible to work without considerable addition of salt, and the process is largely a pickling one, the hydrolyzed acid of the aluminium salt combining with the skin and leaving a basic salt which is also absorbed, the quantitative relation between the two independent actions depending on the relative concentrations. If, instead of alum or normal aluminium sulphate, a basic alumina solution is used, salt can be reduced or dispensed with, and the tanning action depends less on pickling and more on the fixation of alumina. What has been said about alumina tannage applies with little variation to tannage with chrome and iron salts.

As regards the fixation of alumina and chrome, there is little doubt that in the first instance it takes place in the form of basic insoluble salts and is largely physical. The more basic a solution of these metals and the more readily and completely it is precipitated by the withdrawal of a further portion of acid, the more heavily it tans. If we imagine a normal salt to diffuse into the skin, and its acid to combine with the amino group of the proteid, then the remaining insoluble basic salt must remain precipitated in and on the hide fiber. Whether this is the final stage may be doubtful. Wilson, in a recent paper on "Theories of Leather Chemistry,"[16] suggests that ultimate combination takes place with the carboxyl group, and this view seems well in accordance with known facts. A. L. Lumiere[17] has shown that the maximum amounts of chrome and alumina which can be fixed by gelatine accord well with this view; and Wilson points out that if, as he supposes, the ultimate gelatine molecule is monacid and monobasic, a divalent ion such as $Ca^{\cdot\cdot}$, joined to two gelatine molecules, should exert only the same osmotic pressure as the monovalent $Na^{\cdot}$, and hence its swelling effect should be much less as is known to be the case; while the trivalent $Al^{\cdot\cdot\cdot}$ or $Cr^{\cdot\cdot\cdot}$ should swell still less and be yet more easily repressed; and that, therefore, chrome or alumina gelatinates, if they exist, should be very stable and insoluble compounds. It is well known in practice that change in the direction of stability gradually takes place on storing or "ageing" alumed leather, and probably the same is true of chrome, though not so easily demonstrated.

[16] J. A. L. C. A., 1917, 12, 108.

[17] *Brit. Jour. Phot.*, 1906, 53, 573; Abst., *J. S. C. I.*, 1906, 25, 770.

Vegetable tannage appears to be of a more colloidal or physical character than that with alum or chrome. Tannins, like the proteids, appear to form colloidal, rather than true ionic solutions, and the particles are negatively charged, going to the anode in electrophoresis. Whether the change is due to ionization or to the fixation of an electrolyte ion is immaterial for our purpose. The gelatinous fibers, as we have seen, take a positive charge in acid, and a negative one in alkaline solutions (v. s.). Hence in faintly acid solution, which produces the strongest positive charge, they attract and precipitate the tannin particles, while in alkaline solution no tannage takes place and in those too strongly acid, the tannins themselves are precipitated.[18] In fact, such colloid precipitations due to electric charges do not seem to differ in principle from ionic reactions though owing to the varying size of the particles and of their charges they are less definite and quantitative. Whether ultimately any closer combination with the fiber ensues, as is suggested in the case of mineral tannages, remains for the present uncertain, but in long-continued tannage there is a further deposition of difficultly soluble matters on and between the fibers by forces generally called "adsorption." We may thus divide vegetable tannage into two stages, in the first of which the tannins combine electrically or chemically with the fiber and render it insoluble, and in the second matters are deposited upon it which add to the weight and solidity of the leather; but of course the two stages overlap in time, and the different qualities of leather produced by different tannages are largely due to their relative proportion, and the amount of precipitable matter which the tanning materials contain. It does not appear that the same affinities are saturated in mineral and vegetable tannages—chromed leather will fix as much vegetable tannage as raw hide, and *vice versa;* and corresponding differences occur in their behavior to dyestuffs.

Besides the mineral and vegetable leathers there is a third class which demands consideration. If raw skins are fulled with oxidizable oils, their water is gradually expelled and replaced by the oil, and if the skins are now allowed to oxidize (which they do with considerable liberation of heat and of acryl aldehyde and other volatile products), and are then freed from unfixed oil by

[18] *T. C. S.*, 1916, 109, 1329.

pressing and subsequent washing with alkaline solutions, such leathers as "chamois," "washleather," "buckskin," and "buff-leather" are the result. Oil leathers, like chrome leathers, are very resistant to hot water, and also to hot soap or alkaline solutions, and may even be shrunk or "tucked" to increase their thickness and solidity by dipping in these liquids at boiling temperature. Their resistance to hot alkaline solutions, in which all oxidized oil products are soluble, proves that something more has occurred than a mere coating of the fibers with oils, but a full explanation has not yet been given. Since aldehydes are known to produce insoluble conjugated products with hide fiber, the explanation that acryl aldehyde (derived from the glycerine by dehydration) was the active agent was a plausible one, but is negatived by the recent knowledge that equally good leathers can be made with the free fatty acids alone. This, however, does not altogether disprove the aldehyde theory, since the unsaturated oils which alone will chamois are apt on oxidation to break at a double linkage with the production of higher aldehydes. Another possibility is that these oils, which are more or less colloid, form emulsions of which the particles are electrically charged, and which combine with the fiber in the same way as the tannin particles may be supposed to do, though probably with an opposite charge (v. s.).

The oil squeezed out and known as moellon or degras is a natural emulsion, and finds wide use in leather-dressing for the "stuffing" of light leathers. This stuffing, the primary object of which is to lubricate the fibers and make the leather supple and water-resisting, may in many cases be also regarded as a supplementary and partial oil-tannage. The fats are applied to the moist leather either by hand as a pasty mixture of oils and harder fats, or in a melted state in a heated rotating drum. In the first method the main effect of the harder fats is to retain the mixture on the surface until the oils are absorbed. The water in the leather lowers the surface tension between oil and leather at the interface, and as the water dries out the oil replaces it by capillarity, leaving the harder fats outside. The surface tension of the various fats with regard to water and their consequent easy emulsification is thus of great practical importance.

A third way of applying fatty matters to leather much used for chrome and other light leather, and called "fat liquoring," consists in drumming the skins with a prepared emulsion, which at first was the alkaline liquor from the washing of oil leathers, but is now usually an artificial mixture of oils and soaps, though occasionally acid emulsions are employed. It has been found that sulphonated oils, especially castor and fish oils, have extraordinary emulsifying powers even on hydrocarbon oils, and the writer has examined a commercial product containing 80 per cent. of mineral oil, which yet was perfectly and spontaneously emulsifiable when poured into water. The question of surface tension at interfaces and against solid surfaces is one of much technical importance, and probably its effect on adsorption is greater than that of the Willard Gibbs law that "substances which lower surface tension accumulate on that surface." The action of protective colloids on metallic sols has been explained as due to the fact that the surface tension of the medium at the metallic surface is greater than the sum of the tensions of the medium and the metal with regard to the protective colloid, which, therefore, spreads in a thin film between them. This coating of the metal by the colloid is of course an adsorption; and a similar action may account for many cases of the latter which are called "anomalous," that is, to which the Willard Gibbs law does not apply.

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"Die phflanzliche Gerbstoff-Kolloid: Eine Theorie ihrer Zusammensetzung und Wirkung auf Kolloidchemischer Grundlagen."

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Procter, H. R., and Wilson, J. A., *J. S. C. I.*, 1916, 35, 156, and *L. Coll.*, 1916, 2, 56.
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Nihoul, E., *L. Coll.*, 1916, 2, 178, 190. (Eng. abst., 227.)
"Tannage a l'alun."

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"Analysis of Limed Pelt."

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Wood, J. T., and Law, D. J., *J. S. C. I.*, 1916, 35, 585.
"Note on the Unhairing Process."

ABSTRACTS.

Partial Acylation of Alcohols and Sugars. Derivatives of d-Glucose and d-Fructose. E. FISCHER and H. NOTH, *Berichte,* 1918, 321-352; *J. C. S.*, 1918, i, 225-227. Preparation and properties of interesting derivatives such as benzoylglucose, di- and tetra-benzoylglucose, tribenzoylglucose, galloylfructose (crystalline), etc.

Effects of Electrolytes on Gelatin. Effect of Salts on the Precipitation of Acid and Alkali-Gelatin by Alcohol. Antagonism. W. O. FENN, *J. Biol. Chem.*, 1918, 439-451; *J. C. S.*, 1918, i, 240. The effect of

salts,* used with acids or alkalies, or the precipitability of gelatin by alcohol, is to increase or diminish it according to the valency of the ions of the salt. Univalent ions, as in sodium chloride diminish the effect of both acids and alkalies, while bivalent or tervalent ions decrease the effect of alkalies, but increase that of acids, except at high concentrations of acid or salt, when the effect is diminished. Bivalent or tervalent anions decrease the effect of acids and increase that of alkalies except at high concentrations. These results are in some ways analogous to the antagonistic effects of certain electrolytes in biological phenomena.

Ionization of Proteins. J. LOEB, *J. Biol. Chem.*, 1918, 531-549; *J. C. S.*, 1918, i, 240-241. The influence of neutral salts on the swelling of gelatin is of a stoichiometrical character, and the inhibition of additional swelling by a salt is due to the diminution of the electrolytic dissociation of the metal-protein compound first formed.

Analysis of Logwood Extracts. G. SAVINI, *Ann. Chem. Applicata*, 10, 26 (1917); *Col. Tr. Jour.*, 4, 81 (1919). Vegetable coloring extracts have increased in value owing to war conditions. Logwood extract is the most important of these natural dyestuffs. The complete analysis of this substance necessitates the determination of the following: Water, ash, coloring and non-coloring substances, insoluble substances and tinctorial power. The presence of adulterants must also be determined, those chiefly used being molasses, glue, dextrin and tannin extracts. For the determination of water, take 5 grams of the material, dry in an oven for 6 hours at 105° C. in a platinum dish of 10 centimeters diameter. For the determination of ash use the residue from the water determination. An enormous swelling usually accompanies the beginning of carbonization, and to avoid this the following process is recommended: The dish with the residue from the water determination is put in the oven for 1 hour at 105° C., then the temperature is gradually raised to 170°-180° C., after which carbonizing is completed directly over the flame. Regulating the temperature so as to avoid fusion of the ash, especially with extracts adulterated with molasses, introduce the dish into the muffle. The determination of the sugars is difficult because the solutions obtained through the use of basic lead acetate, and also sodium sulphate and phosphate, rapidly assume in the light an intense blue color that renders impossible the reading of the saccharimeter. The following method is recommended: 40 grams of the fluid extract or 20 grams of the dry extract are dissolved in about 100 cc. of boiling water, in a tared flask of 200-300 cc. While agitating the hot liquid add to it not less than 50 cc. of lead acetate. Cool the solution rapidly, bringing to a volume of 200 cc., then adding 15-20 cc. of water to allow for the volume of insoluble substances (20 cc. for extracts containing less than 10 per cent. of sugar, 15 cc. for extracts containing over 10 per cent. of sugar). Shake and filter rapidly, pouring 100 cc. of the filtrate into a 150 cc. flask, and adding a concentrated solution of sodium sulphate and phosphate to com-

plete the precipitation of the lead. Bring to volume and filter. Treat the liquid thus obtained in the usual manner, inverting a part and determining the sucrose by Clerget's method and finally the reducing sugars by the chemical method. The determinations are exact, and limpid and colorless liquids are obtained which remain so for a considerable time.

Clarification of the liquor with hydrated iron oxide, proposed by Cochenhausen, is not practically possible for saccharimetric determinations. The presence of molasses may be shown by the following test: Heat a little of the extract in a dish with boiling water, and the characteristic odor of molasses may be perceived in amounts even as small as 5 per cent. In dry extracts the presence of considerable quantities of molasses causes a change of color and a pitchy consistency. Pure extracts have a decidedly reddish brown color, are friable and do not soften except at high temperatures. Those which contain much molasses take on a clear brown color and soften between the fingers; in time, even at ordinary temperatures, or in warm weather, they become fluid and take the shape of the containing vessel. The brown color of the ash of the extract often indicates the presence of molasses, according to Cochenhausen. Savini found, however, that with extracts containing as high as 20 per cent. molasses, the ash was fairly white. The easy fusibility of the ash of extracts containing molasses, on account of their high content in potassium salts is a good indication of the presence of molasses. The above crude tests are only qualitative.

Savini worked out a method of determining molasses, based on the fact of the small amount of potassium carbonate in logwood extract; the ash amounts to about 2 per cent., of which one-fourth is potassium carbonate. The following method was used: The ash obtained in the determination of mineral substances is lixivated with boiling water, and filtered through a small filter. Wash the dish and filter well so as to use not more than 100 cc. Cool, titrate with a one-tenth normal solution of sulphuric acid, using methyl orange as indicator. The results should be expressed as cubic centimeters of tenth normal alkali per 100 grams dry extract, from which may be calculated the corresponding amount of potassium carbonate. The method gives satisfactory results and in only one sample of fluid extract was there wide divergence between volumetric and gravimetric figures; this was due to adulteration with tannin extract and consequent presence of much sulphuric acid. Taking 0.4-0.5 per cent. as being the amount of potassium carbonate in pure logwood and 6-7 per cent. as that of molasses, the estimation may be made of the amount of the latter in logwood extract. Assuming that molasses contains an average of 50 per cent. sucrose this estimation should be checked by the amount of sucrose found. If a certain quantity of sucrose is found in a sample of extract and the amount of potassium carbonate is equal to that of the pure extract, then it is evident that sugar has been added as such (perhaps raw sugar) and that molasses is not present. The analyses are given of fourteen different samples of dry and liquid commercial logwood.

Rapid Determination of Resin in Soaps. V. FORTINI, *Ann. Chim. Applicata*, 102-8 (1917); *J. S. L. T. C.*, 3, 27 (1919). The method is based on the different behavior of the fatty acids and resin acids when nitrated, the former being aliphatic acids while the latter are aromatic compounds. Two grams of the mixed acids prepared from 20 grams of soap are transferred to a 100 cc. separating funnel containing 50 cc. of petrol ether (boiling point 40°-70° C.). When as complete solution as possible has been attained add 10 cc. of nitric acid solution prepared by mixing 25 cc. fuming HNO_3 (1.52) and 75 cc. HNO_3 (1.48), and a few crystals of urea to render the acid colorless. Agitate the whole for 2-3 minutes, cooling if necessary. The acid layer becomes red, then a reddish brown, and the ether solution becomes greenish, then yellow, which marks the end of the reaction. Allow to separate and tap off the acid layer. (In the presence of much resin a liquid ring of an intensely red-brown color will form at the junction of the two liquids.) The nitration is repeated using 5 cc. of the nitric acid, then the ethereal solution is washed with ordinary HNO_3 and finally with water, after which it is filtered. The filtrate is collected in a weighed dish and the paper washed with a little petrol ether. The ether is then evaporated, the residue dried at 100° C. and weighed. The weight of acids found gives the fatty acids in the quantity taken. The resin acids are found by difference.

Note on Kjeldahl's Method for the Determination of Nitrogen as Applied to Gelatine. H. G. BENNETT and N. L. HOLMES, *J. S. L. T. C.*, 3, 24 (1919). Whereas the digestion of gelatine differs from vegetable-tanned leather in the small amount of carbonaceous matter to be oxidized, the author thought the results of this work would be of interest to the Leather Analysis Committee of the S. L. T. C. The work was started owing to difficulty in obtaining concordant results. It was found that the clearing of the liquor being digested was no criterion of complete hydrolysis and it was desired to find the shortest reliable time and method in which the same could be completely effected.

Four series of experiments were made as follows: (1) About 0.25 gram of gelatine weighed and transferred to digestion flask (200-250 cc.), 10 cc. of concentrated H_2SO_4 added and the mixture boiled until it became colorless. This required from 3½ to 4 hours. The liquid was cooled, diluted and the ammonia distilled off. Other experiments of this series were run under the same conditions except that the boiling was continued from 1 to 20 hours after the solution became colorless. (2) Same as (1) except that when the gelatine was dissolved the liquid was cooled and 2 grams of pure anhydrous sodium pyrophosphate was added, and then the boiling was continued. (3) and (4) Same as (2) except 5 grams of sodium pyrophosphate and 10 grams anhydrous potassium sulphate respectively were added.

On the conclusion of the digestion the solutions were cooled and diluted with water, transferred to a large conical Jena flask and 10 grams of solid caustic soda together with a little pure zinc were added. The

ammonia was then distilled off and collected in 50 cc. of a 3 per cent. boric acid solution (neutral to methyl orange) and titrated with N/5 HCl, whereby only one standard solution was needed.

Time of digestion Hours	1st series Per cent. N	2nd series Per cent. N	3rd series Per cent. N	4th series Per cent. N
4	14.56	14.96	15.15	15.32
5	14.60	——	15.28	——
6	14.68	14.94	——	15.31
7	14.82	——	——	——
8	14.87	14.96	——	15.28
9	14.82	——	15.28	15.27
10	14.90	15.03	——	——
13	14.94	14.96	15.26	——
24	14.90	——	——	——

The author concludes that 10 grams of potassium sulphate for 4-6 hours gives the most reliable results. [This is required by the official method of the A. L. C. A.—ABSTRACTOR.] G. W. S.

Cu-Nao: Its Utilization in Tanning. JALADE, *Bull. Sci. pharmacol.*, 25, Pt. 2, 298-301 (1918); *C. A.*, 13, 673 (1919). The so-called "dry extract" of this common plant (Dio scorea atropurpurea Roseb.) of Indo-China consists of dried slices of the tubers and is not, properly speaking, an extract. Moisture 16.43, tannin 20.20, soluble non-tans 7.07, starch 26.8, nitrogen containing derivatives 3.24, fat 0.32, cellulose 25.94. The tannins were determined in the solution obtained by exhausting with water at 50°, the use of higher temperatures being inadvisable owing to the large amount of starch present. The tannins belong to the pyrocatechol group and give a grayish precipitate with ferric salts. A reddish yellow coloring matter is present. Ash 2.10 per cent., strongly alkaline in water, contains SiO_3 and CO_3, with traces of Al, Fe, Ca and Mg, tests for K were negative. After extraction of tannin the residue might be used as a feed, but the difficulty of drying and the rapid development of molds are obstacles. G. W. S.

PATENTS.

Softening Paper, Leather and Celluloid. Swiss Patent 76,547. J. SIMON and DURKLEIM, Jan. 2, 1918. *C. A.*, 1918, 1,421. The material is treated with glycol, during or after manufacture. *E. g.* (1) in tanning hides, etc., 2 per cent. of glycol, specific gravity 1.12, calculated on the weight of skins, is added to the tanning liquor, and (2) 100 parts leather are treated for 1 hour with a mixture of 2 parts Turkey-red oil soap, 1 part glycol, 6 parts beef tallow, 6 parts leather fat and 2½ parts vaseline, the whole mixture emulsified with 20 parts water, and added to 150 parts water in the vat.

Zinc Sulphide; Lithopone. Engish Patent 114,407. P. COMMENT, May 9, 1917. Zinc sulphide in a white stable form is prepared by calcining a mixture of zinc pentasulphide and zinc sulphate or sulphite with or without alkali sulphate. Barium sulphate may be added to the mixture for calcination in order to obtain lithopone.

Light-proof Lithopone. U. S. Patent 1,260,811. G. RIGG, Mar. 26, 1918. *C. A.*, 1918, 1,517. Lithopone is rendered light resisting by grinding with barium nitrate after furnacing. This converts zinc sulphate to nitrate with simultaneous formation of barium sulphate. U. S. Patent 1,260,812 describes the removal of zinc sulphate from lithopone by treatment with barium sulphide.

Softening Water. English Patent 118,668. E. EDSER, 3, Hillyfields Crescent, Brockley, and S. TUCKER and MINERALS SEPARATION, LTD., 62, London Wall, both in London. Sept. 3, 1917, No. 12624. (Class 46.)

Calcium and magnesium salts or other metallic impurities are precipitated by ordinary reagents, the precipitate being formed into froth with the aid of a suitable frothing-agent, such as oleic acid, soap, eucalyptus oil, or turpentine, and removed by flotation, the process being analogous to the processes of ore treatment described in Specifications 7803/05, 2359/09, 21857/10, and 105,627. Trisodium phosphate or a mixture of hydrogen disodium phosphate and caustic soda are preferred as precipitants for calcium and magnesium salts; but other known precipitants may be used. Soluble salts of copper or zinc may be precipitated with lime or caustic soda and the precipitate formed into a froth with the aid of turpentine.

Journal of the

American Leather Chemists Association

Vol. XIV | JUNE, 1919 | No. 6

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Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members. $5.00 annually; Non-members, $6.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized July 16, 1918.

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NOTICE.

The Ten Year Index of the JOURNAL (Vols. 1 to 10) is now ready for distribution. Copies can be obtained from the Manager and to simplify the handling of this matter as much as possible the remittance should accompany the order. The price of copies bound in brown buckram is $3.00, unbound $2.00.

PRESIDENT'S ADDRESS TO THE SIXTEENTH ANNUAL MEETING.

By R. W. Griffith.

Fellow Members of the American Leather Chemists Association:

This Convention marks the sixteenth annual meeting of the American Leather Chemists Association and it is my privilege, since you have conferred upon me the honor of the presidency of the Association, to welcome you to this meeting, which I hope at its conclusion will record some progress in the advancement of the industry which is our special study.

Since our last meeting, one year ago, the affairs of the world have moved mightily and from the chaos of war the world is making efforts to adjust itself to the ways of peace and attempting to draw such conclusions from its struggles in the war as may be profitable in peace. The affairs of mankind are undergoing a great change. The influence of this change is world wide, and we shall not escape the result, whether it be for good or ill. When the world cataclysm was precipitated and the force of arms sought to dominate, it was a direct challenge to industry which could not be ignored, because war stood in the path of industry. The whole purpose of industry is constructive and aims for the betterment of mankind, but when its right to peaceful pursuits was challenged it gradually turned from its purpose and strove with all its might to crush its adversary. So the great architects of industry, the chemist and the engineer, changed its

course from the constructive efforts of peace to the destructive results of war. The cost to industry was staggering, but the issue was decided and industry prevailed and vanquished the forces of war.

That the terrors of war were increased when the chemist took a hand in it is not denied, and it has been said that science has prostituted herself by the diabolical ingenuity brought to play in warfare, but, on the other hand, these same terrors first introduced by the enemy when applied against them materially contributed to ending hostilities.

There is a curious error so prevalent in the popular mind that chemistry is a branch of science which originated entirely with the Germans, whereas, the fact is, that the Germans contributed nothing to the fundamental principles of chemistry. Their industrial achievements have been principally confined to exploiting the discoveries of other people. So far as the science and practice of leather manufacture is concerned, Germany has contributed nothing to the common fund of knowledge. No one will, however, withhold from the Germans the doubtful credit of being the first to debase the service of chemistry in warfare.

The war is ended and the American chemist can regard with satisfaction his contribution toward bringing about the happy result and he may now return to the pursuits of peace, which have been so fruitful of benefits to industry and the well-being of his fellow man. The American Leather Chemist deserves well of his country no less than his brother engaged in more spectacular work in connection with munition and gas warfare. The requirements of leather for military purposes were enormous and the demand imperative. The failure of the supply of an essential tanning material was no cause for delay in producing leather for military needs, and quality was not to be sacrificed for any reason whatsoever. Substitution and the adjustment of the tanning process to the materials available, under the guidance of the leather chemist, enabled the United States to produce leather on a scale unparalled in the history of the industry, and supply the deficiencies of our Allies with this essential material. The services of the leather chemists to the industry, need no eulogy or defence. His place is established and the progress of the industry is marked by his efforts.

Turning to the consideration of the advancement of leather chemistry towards a more exact scientific basis, we have to record a steady progress; and the laboratory control of the tannery, while still largely empirical, is becoming more exact. The theoretical aspect of the tanning process is receiving more and more attention and this feature of our work should be encouraged, as it cannot fail to be productive of much good which will lead eventually to practical results. There are as many theories as there are processes of tanning, but the fundamental theory of tanning is yet to be established. The application of the principles of colloid chemistry to the tanning process is not only interesting, but is capable of yielding very practical results. The electronic theory of matter is not without great interest to the leather chemist, as the researches into the analysis of leather formation are by no means complete. A well considered theory stimulates vision, which is so essential to progress.

I would take this opportunity to refer to the committee work which is so vital a part of the Association and which has contributed much to the progress of leather chemistry. The investigation of problems by committees is a peculiarly American institution and it is one of which we should be very proud. It provides equal opportunity to all members of the Association to contribute to the common effort and advance the common good, and typifies the spirit of America. A number of committee reports will be presented and discussed during these meetings, and, on behalf of the Association, I wish to thank all those who have so cheerfully and unselfishly given of their time and labor to this good work by serving on the committees. Owing to the pressure of routine work brought about by the war, the number of committees appointed by the Council last year was reduced. I sincerely hope, however, that there will be no further occasion to relax our efforts in committee work, and the co-operation of every member of the Association will be most heartily welcomed.

Our Association is fortunate in the possession of a JOURNAL which is not only well printed, but well edited. I must confess, however, that so far as contributions from our own members is concerned, we are sadly lacking. Each of us must try to realize the individual responsibility which rests upon us to maintain the high standing of our JOURNAL. May I impress upon you the

urgency of this matter and secure your individual co-operation?

Since our last meeting, it is my great pleasure to announce that the mutual membership arrangement entered into with the Society of Leather Trade Chemists has been consummated. Under this arrangement members of both organizations have the privilege of obtaining the JOURNALS issued by both Associations at a nominal advance in the annual dues. This exchange of JOURNALS provides an excellent opportunity for the advancement of mutual interests and is a step towards creating a good understanding with our friends across the sea.

What of the future of the leather chemist? It is not presumption to say that the future of the leather industry is in his hands. Not many years ago the tannery chemist occupied a very obscure place in the general scheme of things pertaining to the tannery and he was regarded with curiosity and suspicion, but to-day, in the most progressive tanneries, all works' operations are controlled from the laboratory and the friendly counsel of the chemist is sought on all the practical problems which arise. The service of the leather chemist is no longer regarded as a luxury, but has become a vital necessity where economical production and the highest efficiency are required, and economy and efficiency are to be the watch-words of the leather industry if our country is to maintain its supremacy in leather production. But it is not to be supposed that the chemist exercises any of the powers of witchcraft, before which all tannery troubles disappear. The very nature of progress leads the seeker into the unchartered seas of knowledge, on which he must mark his own course to the port of his ambitions. A chemist is one who has been trained in the fundamental principles of knowledge which is called science, and it is in his power of observation and in his ability to apply the established laws of nature to the problems of the industry that his usefulness is recognized, but, in common with the rest of humanity, the chemist develops his real value with experience.

As an Association of Leather Chemists, we have a very real mission to perform, not only to our industry, but to humanity. Let us not lightly regard our duties and our responsibilities; and let us remember that the purpose of our mission is to serve and let our service be real in its loyalty to our Association and in its devotion to the high ideals which dominate our national life.

NOTES ON AUSTRALIAN TANNING MATERIALS AND THE MANUFACTURE OF SOLE LEATHER.*

By F. A. Coombs.

A number of workers at the Sydney Technical College have just completed a series of comparative tests which were expected to give results directly related to the leather-producing properties of Australian tanning materials.

Australia has large supplies of tannins in the kinos and barks of the numerous species of eucalypts. The tannins in the barks of *E. sideraphloia* were tested by the process which has been described in previous papers.[1] The results show that under normal conditions it would be extremely difficult to get these tannins to penetrate into the center of the hide. In this experiment the standard tannage (wattle bark tannins) gave the usual result and the sections were "struck through" at the end of the fourth week, but at this stage the sections in the liquors obtained from the bark of *E. sideraphloia* showed a broad untanned streak in the center of the hide. After the sections had been in the tan liquors for ten weeks it was found that the eucalyptus liquors had made no perceptible progress under what was considered to be normal conditions, and, therefore, a continuation of the experiment was not considered necessary.

A mallet bark (*E. occidentalis*) tannage gave a hard brittle leather after drying from the wash pit. The same leather was "damped back," drummed with weak liquor for one hour, and finished as sole leather. It was then free from any brittleness.

This change might be considered to be due to a large amount of uncombined tannins, etc., which would have a tendency to make the leather brittle, and one hour in the drum would remove the soluble substances and enable the leather to dry to a normal and mellow condition. While this may be true to a certain extent, yet it is probable that the mechanical action in the drum broke up the leather and was an important factor in reducing it to its mellow state. However, this is the only good leather the author has seen which was tanned by a straight eucalyptus tannage.

The barks of the eucalypts and their exuded kinotannins are not popular with Australian tanners. In a few of the sole leather

* Reprinted from J. S. C. I. **38**, 701 (1919).

[1] This JOURNAL **12**, 158 (1917).

tanneries a small proportion of mallet bark is used, and the results appear to indicate that this bark improves the color obtained from the local tannage, but while it gives a firm leather, there is always a tendency to a brittle grain if the tanning process is confined to the pits, and it increases the time required for the various liquors to penetrate into the center of the hide. If mallet bark, with its high percentage of tannins capable of imparting a good color to leather, is not used to any great extent in Australia, it does not seem probable that the barks or kinos of other eucalypts will be used in large quantities unless it can be shown that they have an increased value owing to their special leather-forming properties. The extract from mallet bark contains a low percentage of non-tannin matters and, therefore, it is an ideal cheap adulterant for mixing with extracts that have better leather-forming properties. Probably a large portion of the mallet bark exported to other countries has been used for this purpose.

The eucalypt tannins, especially mallet, may give much better results when they are used in a drum tannage, but at present they cannot be considered an important factor in the production of Australian leather.

Wattle bark is the principal tanning agent used by Australian tanners, and while the supplies of this material are equal to the demands, other tanning materials without special leather-forming properties are not likely to be used in large quantities. This bark is used for the production of all classes of leather and its general leather-forming properties are superior to those of any other known Australian tanning material. It is doubtful if a more useful catechol tanning material is produced in any part of the world, and when the natural supplies of tannins are exhausted the wattles can be cultivated to meet the demands of tanners. A straight wattle tannage produces a mellow leather which is suitable for the currier, and it can be converted into kip, bag, strap, harness leathers, etc. A mixed tannage of wattle and imported tanning materials, such as gambier, myrobalans, sumac, and valonia, is used by some tanners for the production of the above leathers, but in all cases the wattle tannins are in excess of the sum of all the others.

Previous experiments indicate that the tensile strength and elasticity of the wattle-tanned leather is greater than that of any

leather tanned with other Australian tanning materials. If it be desirable to reduce the elasticity or stretch of wattle-tanned belting leather, this leather could be tanned with a mixed tannage of wattle and pine or wattle and mangrove. These mixed tannages would bring about a slight reduction in the tensile strength, but if skilfully controlled they should not make any appreciable difference in the resulting leather. Leather tanned with wattle tannins does not offer a great resistance to the penetration of water. Pine and mangrove give better results than wattle, and pine is superior to mangrove.

From the percentage of fixed tannin calculated on the hide substance ("degree of tannage") we find that the pine tannins return the greatest percentage of insoluble leather. In other words these tannins have the best weight-producing properties, mangrove being second and wattle third. It has been shown that the resistance to water is proportional to the amount of fixed tannin. It would be extremely difficult to obtain wattle and pine leathers suitable for comparative tests and both containing the same amount of fixed tannins, hide substance, etc. One of the best tests for the water-resisting properties of any tannage is to "damp back" the dry unrolled leather to a condition suitable for splitting, drum stuffing, or setting up. It is not necessary to go into the details of this process. Briefly the wattle leather is quickly and easily prepared for this work. The pine leather appears to resist the penetration of water into the fibers and apparently never reaches that mellow condition known by the "feel" which is so hard to describe but is well known to all practical men who handle wattle-tanned leather for the manufacture of dressed goods.

Wattle tannins when used as the greater portion of a suitable mixed tannage give good results in the manufacture of sole leather. Under the heading of Australian tanning materials, one might say that the most important work at the present date is to help in the expansion of the wattle-bark industry and secure for the Australian tanning industry the necessary supplies for its future requirements.

The tannin values of wattle bark as supplied to the tanners range from 30 to 39 per cent. Adelaide bark (*Acacia pycnantha*) with few exceptions contains 34-39 per cent. tannin. Mr. G. H. Maiden describes the "*Acacia decurrens* group of wattles" in

"Forest Flora of N. S. Wales." He has reduced what are described by some botanists as species to varieties of *A. decurrens*. According to the same authority there are a number of varieties of *A. decurrens* and the following contain considerable amounts of tannin in their bark: *Acacia decurrens*, varieties *normalis, mollis, pauciglandulosa, Leichardtii,* and *dealbata*. The variety *mollis* (*A. mollissima*) appears to be the best of the *decurrens* group and the bark contains from 31 to 39 per cent. of tannin. This variety is hardy and probably the most suitable for cultivation. Some of the other varieties are not much inferior to *mollis*, but it is extremely difficult to procure commercial samples and, therefore, it is impossible to give their true tannin values. Generally the barks sold in Sydney are mixtures of *normalis* and *mollis* varieties and the tannin values are above 30 per cent. excepting when the sample contains a large proportion of *dealbata*. Commercial samples of *dealbata* have returned 20 per cent. of tannin. Apparently there is no great botanical difference between the five varieties named above, but there is a marked difference in the tannin value of *mollis* and *dealbata*.

In Australia the supplies of wattle bark have not been equal to the demand, and large quantities of this bark have been imported from South Africa. The South African bark, reported to be *decurrens* varieties with *mollis* predominating, differs from the Australian bark from the same species. It appears to contain a larger proportion of the thin bark from the young branches, and some tanners say that it does not give up its tannin so freely during the leaching process. A number of our local tanners prefer to keep the wattle bark for several months before using it. They claim that their practical experience has shown that they leach more tannin from the old bark. One tanner suggests that the solubility of the tannin increases when the bark is allowed to age. The tannin in bark that is stored for several months generally changes to a red color. This would probably bring about a decrease in the solubility of the tannins. The improved results obtained might be due to the change that would take place when the moisture in a bark is reduced to a low percentage. Under these conditions the cells, etc., would contract, and this contraction, in conjunction with the subsequent swelling when the bark is placed in water, would cause ruptures and strains which would

help the tannin to diffuse out of the bark. South Australian bark (*A. pycnantha*) is supposed to have better leather-forming properties than the bark from Australian and South African varieties of *A. decurrens*. This difference could probably be traced to the methods used to prepare the bark for the markets. The South Australian bark industry is controlled by men who are far superior in systematic methods and general knowledge of the industry to other bark strippers in Australia and South Africa. South Australian bark is generally ground in the mill before it is sent to Sydney. This bark must be dry before it will pass through the mill, so that the men who strip and prepare this bark are forced to reduce the water to a low percentage and, therefore, no bark is exported before it is thoroughly dry. Bark stripped in New South Wales and South Africa is generally exported as chopped bark and it often reaches the tanner with a high percentage of moisture. The former may show signs of moulds and the latter sometimes contains green bark from young branches. The red appearance of South Australian bark is probably due to the bark being stored for a longer period after stripping. It generally contains more red tannins, which would probably increase its weight-giving properties and justify the claim of certain tanners that this bark gives the best weight returns. The basil tanners, who have to consider color as the most important factor, generally prefer the chopped barks from New South Wales and South Africa, but there is no great difference in the color of the leather tanned with these barks.

The pine barks have not been used in large quantities by Australian tanners. Much credit is due to Mr. Greatrex for his great effort to place this bark in the Australian sole leather tanneries. He has stripped large quantities of the bark (*Callitris calcarata*), and analysis would appear to indicate that when this bark is rossed the tannin values are above 20 per cent. Samples taken from a ten-ton lot gave 23.5 per cent. of tannin. The general opinion is that before these tannins become popular with tanners they must be sold in the form of an extract.

We have described the valuable water-resisting properties of leather tanned with pine tannins, and there is no doubt that the pine bark used in a mixed tannage with wattle bark would produce a sole leather with water resisting properties that are superior to results obtained with a straight wattle tannage. A

straight pine tannage produces a red leather, inclined to be harsh, with splendid water-resisting properties and giving good weight returns. Small quantities might be considered useful for dressed leathers but practical experience does not support this.

The mangrove tannins sold in Australia consist largely of a mixture of three genera, *Ceriops, Rhizophora,* and *Brugiera.* This bark produces a red leather which does not reach the same high standard for resistance to the penetration of water that has been noted for pine-tanned leather. The tannins from the bark of *Ceriops* are not so red as the tannins from *Brugiera,* and *Rhizophora* appears to occupy an intermediate position. One would expect these tannins to be in the same order for the "time for penetration" and the production of a soft leather. As a mixture they are slower than wattle tannins, and *Brugiera* used alone would probably produce a harsh leather with a tendency to a brittle grain.

The value of any tanning material will depend on its leather-forming properties and the cost of producing tannin in solution. The mangrove tannins are inferior to the wattle tannins in their general leather-forming properties. Mangrove, when used alone for the production of sole leather, gives very fair results, but the water-resisting properties are apparently not up to the standard required for this leather. When black labor is available large quantities of mangrove tannins can be obtained in solution at a cheaper rate than from any other tanning material, and this appears to be the reason for their use by tanners. The mangrove tannins appear to have no outstanding feature which would make them valuable for the production of some special leather. The tanners' problem is how much can they use of this cheap tanning agent without making any appreciable difference in the quality of their leather. At present mangrove tannins are generally used as a small portion of a mixed tannage for the production of sole leather, and if the resulting leather is red the color can be improved by using a weak solution of titanium salts. The mangrove tannins vary from a yellow to a deep red color; reducing agents such as sulphur dioxide, temporarily remove a portion of the red color. The tannin values of a few commercial samples of this bark range from 30 to 37 per cent. The bark from British Papua has not given the same high tannin values as the bark from

North Queensland. Probably only the best of the mangrove bark in certain localities has been stripped and placed on the markets. The tannin values may be lower when larger quantities of these barks are stripped in the above districts. The author has taken samples for analysis from Cairns and Cooktown in Queensland, and on the coast of Papua near Yule Island, and the results seem to indicate that this bark could be supplied to the tanner in large quantities and the tannin values should not be expected to fall below 30 per cent., while some lots would reach 37 per cent. for rossed bark.

The tanning process for sole leather may be divided into two parts. The first consists of converting the raw pelt into leather, and the second would cover the addition of weighting and filling agents which in some cases improve the quality of the leather. The time required to convert the pelt into leather by the aid of a mixed tannage with wattle bark predominating is generally about four to five weeks, and this part of the process ends when the tannin has penetrated into the center of the hide. If acid be employed for plumping purposes its use should be restricted to the early stages of the first part of the tanning process. It has been shown that the tensile strength of a leather decreases when it has been fixed by tannin in a swollen condition, so that the use of acid to make leather thicker adversely affects the wearing quality of the leather if, as the author's experience seems to indicate, the resistance to wear is proportional to the tensile strength. When an experienced buyer is examining sole leather he generally notes if the leather be "firm" or otherwise. It would be difficult to give a scientific explanation of this factor. As a general rule one could say that starting with a good hide and tanning it by a process known to give good sole leather results, one might expect to have a hide of leather which would be firm in the butt but not firm in certain other portions of the hide. There are a great number of factors which assist in the production of a firm sole leather, but it is only proposed to deal here with one, as it may justify to a certain extent the use of acid for the production of this leather.

It has been shown in a previous paper[2] that the acid is responsible for a harder, more rigid, or firmer leather, which appears

[2] This JOURNAL 13, 255, (1918).

to offer a greater resistance to water penetration. Sometimes it is necessary for a tanner to "damp back" his dry leather, and the quickest way to obtain this result is to place the leather with water in a revolving drum. While the drum is in motion the leather is continually falling from the shelves to the bottom. This mechanical action breaks up any thin film, etc., which forms a temporary barrier to water, expels the air from the capillaries by a pressure which only lasts for a fraction of a second, and leaves a vacuum which is immediately followed by a flow of water into the leather. The rate at which water is absorbed by leather is proportional to that mechanical action which is responsible for stresses which adversely affect the compactness of the leather. Under natural wearing conditions sole leather is exposed to this mechanical action, and the resulting strains decrease with a firmer or more rigid leather.

Apparently there is some evidence to justify the use of acid in the manufacture of sole leather that is required for a wet climate, but it is doubtful if it has any value if the leather is tested under conditions natural to a dry climate. The tannage of certain imported sole leathers consists of a high percentage of myrobalans and valonia, and under these conditions the acidity of the liquors would be high. These leathers do not always give good wearing results under dry weather conditions common to Australia. They are too rigid for comfortable walking and the fiber is inclined to be brittle. Australian tanners who use myrobalans and valonia generally work on the safe side, but it should be noted that the addition of acid or acid-producing substance in conjunction with these tanning materials may produce a harsh, brittle fiber, especially in the center of the hide.

Fixed tannin in excess of the amount required to convert the hide into leather may be classed as the most important filling agent known to tanners at the present time. The second part of the process of tanning sole leather has for its object the partial filling of the leather with fixed tannins, and to obtain successful results the tanner must use strong tan liquors and suitable tannins, and the leather must remain in the liquors for several weeks. This is the more costly part of the tanning process.

There can be no doubt as to the value of layaways for increasing the amount of fixed tannin as found by analysis when the

unleached bloom-yielding tanning materials are placed between the hides. Procter[3] states that the same rule holds with hemlock, quebracho, and mimosa, which yield no bloom but difficultly soluble tannins (reds or phlobaphenes). He states that in contact with the hides the small proportion of these reds which is soluble in the liquors is replaced from the material as rapidly as it is absorbed by the leather, while when liquors or extracts only are used the greater part of these solidifying and weight-giving constituents remains unutilized in the spent tanning materials. So far as wattle bark is concerned we have no practical results to show that this is the true theory for these layaways. Before accepting the above theory one must be prepared to acknowledge that the amount of fixed tannins increases as the solubility of the tannins decrease, or that the hide would fix difficultly soluble tannins (reds) in preference to the easily soluble tannins. This appears to be correct and in accordance with practical results. It would now appear that the fixed tannins were proportional to the percentage of reds in the tan liquor. Procter's theory appears to be that at constant temperature and concentration the amount of reds in solution will be constant and any loss, such as combined tannin, etc., will be renewed from the bark. The reds in tan liquors are proportional to the temperature maintained during the process of extraction. Some of the reds pass out of solution when the liquors cool to ordinary temperature, but the percentage would still be much higher for a hot-water extraction when compared with results obtained by extraction at ordinary temperature.

The layaways are generally made up of ground bark and a liquor taken from leaches where hot water is used in the process of extracting the tannin from the bark. Tannin is extracted from the bark in the layaway at ordinary temperature, but Australian experience seems to indicate that the reds are left in the bark. If it is desirable to get the maximum amount of reds in the leather, the tanner should not place the bark in the layaway, but he could use that bark in the leaches and increase the concentration of the liquor by the amount of tannin extracted from this bark. Then one would expect a stronger liquor which would maintain a greater percentage of reds when it is brought in contact with leather.

[3] "Principles of Leather Manufacture."

There are other important factors connected with layaways, such as the large number of hides that can be placed in a pit and the small volume of liquor required to cover them, also the extra labor required in handling the hides and removing the bark to the leaches. Remove the layaways (which appears to be feasible as regards Australian tanning materials) and the tanning and leaching processes become less difficult to control.

There is no reason why the fixed tannins in excess of those required to convert the hide into leather should not be replaced by other substances as filling agents. A vegetable-tanned leather filled with a plaster substance insoluble in water might be expected to give good wearing results in a dry or wet climate, but, like chrome-tanned sole leather, it would differ from the present vegetable-tanned leathers which are capable of being "damped back" to a pliable condition. This wet, pliable condition enables boot manufacturers to work the leather to the required shape. The value of "damping back" is only known to tanners and leather workers, and it must be noted that it would not be possible to obtain this result with a leather which would completely resist the penetration of water. Water solubles must be reduced to a minimum and sulphuric acid entirely removed from the vegetable-tanning process before any great improvement will be made in the quality of sole leather.

Leather which contains a medium percentage of fixed tannin and solid fats and also a low percentage of water solubles would probably give the best results without bringing about any great changes in the present methods of tanning sole leather, but quicker returns and better results are possible when a substitute is found for the excess of fixed tannins.

A chrome-tanned sole leather filled with waxes, etc., gives better wearing results than the average vegetable-tanned sole leather. The former does not contain any substance similar to the excess of fixed tannin which is considered such an important constituent of the latter. If the vegetable-tanned leather were treated with waxes, etc., after it has passed through the first part of the tanning process, the resistance to wear might equal that of the chrome leather. Tanners would then have to consider which is the cheaper process. The basic chromic solution would take one week to convert the hide into leather, and vegetable tannins

would require four weeks to do the same work. This is a big advantage for the chrome tannage, but it is more than counterbalanced by certain advantages on the side of the vegetable tannage.

When the vegetable-tanned sides of leather have passed through the first part of the tanning process, they can be trimmed and classed to suit the demands of the tanner's customers. The butts can be filled with waxes or fixed tannins. The offal can be "dried out" and sold to various buyers who damp it back and prepare it for various sections of the leather industries. Australian tanners could ship picked sides and offal to London and English tanners would prepare it for their own markets. A large number of tanners who manufacture harness and belting leathers, also make sole leather from their culls, etc., and the sides for these leathers could be sorted out at the stage mentioned above. Now chrome-tanned offal, etc., cannot be shipped and sold for the purposes described under the vegetable tannage because this leather cannot be "damped back." Only the butts are generally used for chrome sole leather and the offal receives a vegetable tannage. So comparing the two tannages it is found that the first part of the process required to produce vegetable-tanned sole leather can be used for the production of all the heavy leathers and the whole side can be tanned as one piece.

The Australian tanners should be prepared to depart from the rigid rules laid down in other countries for the manufacture of sole leather. They should aim at producing, with the aid of Australian tanning materials, leathers that will suit the local climate and the export trade.

The following is a statement of the comparative positions for leather-forming properties of Australian tanning materials, the best material being given first: *Resistance to water-penetration*: Pine, mangrove, wattle. *Color*: Mallet, wattle, mangrove, pine. *Degree of tannage*: Pine, mangrove, wattle. *Tensile strength*: Wattle, mangrove, pine. *Penetration of tannin into pelt*: Wattle, pine, mangrove. *Soft leather*: Wattle, mangrove, pine, mallet. *Elastic properties*: Wattle, mangrove, pine. *Acidity of liquors*: Pine, mangrove, mallet, wattle. *Firm leather*: Mallet, pine, mangrove, wattle. *Percentage of tannin*: Mallet 36-42, wattle 30-39, mangrove 30-37, pine 18-23 per cent.

The local tanning materials used for the manufacture of Australian leathers may be summarized thus: *Wattle*: Kips, etc.; split grains for colors; harness, bridle, strap, sole leathers; belting leathers; basils, book-binding leathers. *Pine and mangrove*: Sole and belting leathers. *Mallet*: Sole leather.

PREPARATION OF LEATHER SAMPLES FOR ANALYSIS. 1919 COMMITTEE REPORT.

By L. E. Stacy, Chairman.

It was the purpose of this Committee to have as many of the different laboratories as possible to prepare samples of leather in their usual way, give a complete description of the machine or apparatus used, and send all prepared samples to one laboratory for comparative analysis with a planed sample of the same leather. Inquiries were made of twenty-eight laboratories, and of this number eight consented to serve on the Committee.

Four different tannages of sole leather were selected, namely, Union, hemlock, scoured oak and Texas oak unscoured. To each member of the Committee three samples of leather were sent with instructions to prepare leather for analysis in their usual way—determine moisture before and after preparation of samples; note if possible, the rise in temperature of samples while in the process of preparation; give a complete description of the machine or apparatus used, and if saws were used, give first the number of saws, second the diameter, third the speed, fourth the character of the teeth, and fifth, manufacturer's number and by whom manufactured.

The leather used by the Committee was bought on the market and obtained in strips from 24 to 27 inches long and from 8 to 10 inches wide. From each strip four samples were made. The strips were quartered and 1 inch planed off both edges of each quarter—the planed leather thus obtained constituting one sample. The two adjacent quarters on each end were sent out as a corresponding sample. The Chairman undertook to prepare twenty-four samples corresponding to each sample sent out, using the same plane and endeavoring to plane as finely as possible. It required from 20 to 25 minutes to prepare each sample. A letter from one member of the Committee enclosing the analysis of

UNION.

Analyst	No.	How prepared	No. of saws	Diameter of saws In.	Speed of saws R.P.M.	Gauge of saws	Moisture			Rise in temperature	Water solubles	
							Before preparation	After preparation	Difference		Average	Dry basis
L. E. Stacy	1	Planed	—	—	—	—	8.86	8.92	+0.06	—	35.53	32.38
T. J. Mosser	1	Sawed	—	—	—	—	9.05	7.10	—1.95	—	36.52	33.95
L. E. Stacy	2	Planed	—	—	—	—	7.85	7.79	—0.06	—	31.50	29.03
J. M. Seltzer	2	Planed	—	—	—	—	8.45	8.49	+0.04	—	30.50	27.92
J. M. Seltzer	2	Sawed	4	10	2400	16	7.59	7.53	—0.06	—	31.58	29.18
L. E. Stacy	3	Planed	—	—	—	—	10.96	10.92	—0.04	—	31.87	28.38
A. C. Orthmann	3	Planed	—	—	—	—	10.77	10.69	—0.08	—	29.56	26.38
L. E. Stacy	4	Planed	—	—	—	—	10.50	10.64	+0.14	—	27.63	24.73
R. E. Porter	4	Sawed	3	10	1500	16	10.85	10.09	—0.76	3.2°—4°C.	27.02	24.09
L. E. Stacy	5	Planed	—	—	—	—	10.66	10.41	—0.25	—	29.40	26.24
J. S. Rogers	5	Sawed	4	10	1605	16	10.00	8.74	—1.26	4°—5°C.	30.63	27.57
L. E. Stacy	6	Planed	—	—	—	—	10.34	10.42	+0.08	—	29.66	26.59
C. M. Kernahan	6	Planed	—	—	—	—	—	—	—	—	30.73	—
L. E. Stacy	7	Planed	—	—	—	—	9.88	9.52	—0.36	—	33.99	30.63
F. H. Small	7	Sawed	3	8	3450	—	10.32	8.84	—1.48	10.5°C.	31.66	28.39

Hemlock.

Analyst	No.	How prepared	No. of saws	Diameter of saws In.	Speed of saws R.P.M.	Gauge of saws	Before preparation	After preparation	Difference	Rise in temperature	Average	Dry basis
L. E. Stacy	8	Planed	—	—	—	—	8.44	8.10	—0.34	—	32.87	30.11
J. M. Seltzer	8	Sawed	4	10	2400	16	7.77	7.76	—0.01	—	34.44	31.78
J. M. Seltzer	8	Planed	—	—	—	—	8.14	8.14	0.00	—	31.66	29.08
L. E. Stacy	9	Planed	—	—	—	—	10.18	10.24	—0.04	—	29.82	26.76
J. F. Mosser	9	Sawed	—	—	—	—	10.01	9.10	—0.91	—	29.88	26.89
L. E. Stacy	10	Planed	—	—	—	—	9.84	9.72	—0.16	—	32.13	29.61
A. C. Orthmann	10	Planed	—	—	—	—	10.04	10.09	+0.05	—	30.93	27.87
L. E. Stacy	11	Planed	—	—	—	—	10.18	10.10	—0.08	—	32.49	29.18
J. S. Rogers	11	Sawed	4	10	1605	16	9.92	9.24	—0.68	4°—5°C.	31.45	28.33
L. E. Stacy	12	Planed	—	—	—	—	10.34	10.24	—0.10	—	31.68	28.41
C. M. Kernahan	12	Planed	—	—	—	—	—	—	—	—	30.70	—
L. E. Stacy	13	Planed	—	—	—	—	10.02	9.96	—0.06	—	29.97	26.97
R. E. Porter	13	Sawed	3	10	1500	16	10.36	10.07	—0.29	3.2°—4°C.	29.73	26.65

UNION.—(*Continued.*)

Scoured Oak.

Analyst	No.	How prepared	No. of saws	Diameter of saws In.	Speed of saws R.P.M.	Gauge of saws	Moisture			Rise in temperature	Water solubles	
							Before preparation	After preparation	Difference		Average	Dry basis
L. E. Stacy	14	Planed	—	—	—	—	9.65	9.72	+0.07	—	33.33	30.11
F. P. Veitch	14	Sawed	4	10	1500	16	8.90	9.00	+0.10	6°C.	33.25	30.29
L. E. Stacy	15	Planed	—	—	—	—	9.96	9.80	—0.16	—	31.27	28.15
F. H. Small	15	Sawed	3	8	3450	—	10.15	9.54	—0.61	9°C.	30.60	27.49
L. E. Stacy	16	Planed	—	—	—	—	10.88	10.72	—0.16	—	30.41	27.10
. S. Rogers	16	Sawed	4	10	1605	16	10.48	9.54	—0.94	4°—5°C.	29.53	26.44
L. E. Stacy	17	Planed	—	—	—	—	10.56	10.15	—0.41	—	31.95	28.58
F. H. Small	17	Sawed	3	8	3450	—	10.15	9.35	—0.80	11°C.	33.29	29.91
L. E. Stacy	18	Planed	—	—	—	—	9.32	9.18	—0.14	—	28.67	26.00
F. P. Veitch	18	Sawed	4	10	1500	16	8.90	9.30	+0.40	6°C.	29.24	26.64

Texas Oak. Unscoured.

Analyst	No.	How prepared	No. of saws	Diameter of saws In.	Speed of saws R.P.M.	Gauge of saws	Before preparation	After preparation	Difference	Rise in temperature	Average	Dry basis
L. E. Stacy	19	Planed	—	—	—	—	9.60	9.30	—0.30	—	32.64	29.51
T. J. Mosser	19	Sawed	—	—	—	—	9.30	7.06	—1.24	—	33.46	30.35
L. E. Stacy	20	Planed	—	—	—	—	10.82	10.66	—0.16	—	28.96	25.83
A. C. Orthmann . . .	20	Planed	—	—	—	—	10.21	10.38	+0.17	—	28.54	25.63
L. E. Stacy	21	Planed	—	—	—	—	9.42	9.64	+0.22	—	32.29	29.25
J. M. Seltzer	21	Sawed	4	10	2400	16	7.24	7.29	+0.05	—	31.81	29.51
L. E. Stacy	22	Planed	—	—	—	—	9.56	9.38	—0.18	—	33.89	30.65
R. E. Porter	22	Sawed	3	10	1500	16	9.80	7.86	—1.94	3.2°—4°C.	33.17	29.92
L. E. Stacy	23	Planed	—	—	—	—	9.91	9.70	—0.21	—	30.07	27.09
C. M. Kernahan . . .	23	Planed	—	—	—	—	—	—	—	—	28.85	—
L. E. Stacy	24	Planed	—	—	—	—	10.06	9.84	—0.22	—	28.18	25.35
F. P. Veitch	24	Sawed	4	10	1500	16	9.40	8.90	—0.50	6°C.	30.72	27.83

the same strip of sole leather by three different chemists, in which each differed widely on almost all the ingredients of the leather, lead the Chairman to undertake to make the water soluble determination on all forty-eight samples, thus eliminating the use of different extraction apparatus, different thimbles and slight differences of temperature of extraction. The following are the results sent in by Mr. Joseph J. Kelly, of the analysis of the same leather as analyzed by the three different chemists using different methods for preparation of samples. Number 1 was planed, No. 2 sawed by a series of five thin 4-inch circular saws with the teeth staggered, and No. 3 was first cut and then ground in a Troemner mill running 100 revolutions per minute.

	1st	2nd	3rd
Water	14.00	14.00	14.00
Oil	0.79	1.16	2.15
Ash	1.36	1.16	1.18
Hide substance	32.99	32.91	30.60
Tannin combined	26.57	25.54	23.41
Tannin free	10.59	9.91	12.18
Non-tannin	14.00	15.63	16.58
Total	100.00	100.00	100.00
Soluble solids	24.59	25.53	28.68
Pure leather substance	59.56	58.15	54.11
Pure leather contains hide	55.40	56.59	56.66
Pure leather contains tannin	44.60	43.41	43.35
Sugar and glucose	8.81	9.07	8.26
Free sulphuric acid	1.20	1.20	2.03

The tables give the results on the samples of leather sent out by Committee:

A study of the tables show that there was practically no loss in the moisture content of the samples when prepared with a plane. The samples prepared with saws with revolutions per minute ranging from 1,400 to 3,450 show a loss of moisture after preparation from 0.06 per cent. to 0.95 per cent. The rise in temperature in these samples was between 3.2° C. and 11° C. The results were not altogether conclusive. But a review of the prepared samples reveals the need of a uniform method of preparing leather samples for analysis. In the case of the planed samples no two chemists planed the leather the same thickness.

The sawed samples, as a whole, seem to possess the same degree of fineness, but a few samples were coarse and contained small lumps of leather.

It is the opinion of the Chairman that the best samples can be prepared with saws, having a diameter from 8 to 10 inches with an approximate speed of 2,000 revolutions per minute. The limit of speed, however, is yet an undetermined factor. To the objection that saws scatter and waste a portion of the sample, throwing particles over the room, Mr. H. F. Small, has well suggested that the saws be so mounted on a shaft that their center will be below the feeding bed. To this, the Committee would also add the need of placing a hood over the saws and allowing only ½ inch open for the feeding space. A machine so arranged wastes practically none of the sample.

COMPOSITION OF A TWO BATH CHROME LIQUOR.

By Earnest Little and Joseph Howard.

The use of the results of analysis of a two bath chrome liquor as outlined by Procter is familiar to all leather chemists. It seems to the writers, however, that in some places these calculations are needlessly complicated. The following simpler calculations are, therefore, offered.

Let us assume that we have six samples of Na_2CrO_4 to which sulphuric acid is supposed to have been added; equal samples of each solution have been titrated with $\frac{N}{10}$ NaOH and $\frac{N}{10}$ $Na_2S_2O_3$, after the addition of KI, with the following results.

	$\frac{N}{10}$ NaOH cc.	$\frac{N}{10}$ Hypo. cc.
1	0	30
2	5	30
3	10	30
4	15	30
5	20	30
6	25	30

The calculations in cases 1, 2, 3, and 5 are similar to Procter's, but as they are very brief, they have been included to make a complete discussion.

1. $0 \text{ cc. } \frac{N}{10} \text{ NaOH}, \quad 30 \text{ cc. } \frac{N}{10} \text{ Na}_2\text{S}_2\text{O}_3.$

If $Na_2Cr_2O_7$ was present it would react with NaOH as follows:

$$Cr_2O_7^{=} + 2OH^{-} \rightarrow 2CrO_4^{=} + H_2O,$$

but as no NaOH has been used it necessarily follows that no $Na_2Cr_2O_7$ is present. The bath is, therefore, made up entirely of Na_2CrO_4 and the calculations are as follows:

$$\text{Grams } Na_2CrO_4 = \frac{Na_2CrO_4}{30{,}000} \times 30 = \text{grams } Na_2CrO_4,$$

$$\text{or } 0.0054 \times 30 = 0.1620 \text{ gram } Na_2CrO_4.$$

3. $10 \text{ cc. } \frac{N}{10} \text{ NaOH}, \quad 30 \text{ cc. } \frac{N}{10} \text{ Na}_2\text{S}_2\text{O}_3.$

The cc. $\frac{N}{10}$ NaOH $= \frac{1}{3}$ cc. $\frac{N}{10}$ "hypo."

$$Cr_2O_7^{=} + 2OH^{-} \rightarrow 2CrO_4^{=} + H_2O,$$

$$Cr_2O_7^{=} + 6I^{-} + 14H^{+} \rightarrow 2Cr^{+++} + 7H_2O + 3I_2.$$

From the above equation it follows that $Na_2Cr_2O_7 = 2NaOH$, and $Na_2Cr_2O_7 = 6I = 6Na_2S_2O_3$; therefore, since a normal solution of NaOH and $Na_2S_2O_3$ each contain one molecular weight per liter, the cc. $\frac{N}{10}$ NaOH $= \frac{1}{3}$ cc. $\frac{N}{10}$ $Na_2S_2O_3$ when the bath is made up entirely of $Na_2Cr_2O_7$.

$$\frac{Na_2Cr_2O_7}{60{,}000} \times 30 = \text{grams } Na_2Cr_2O_7,$$

$$\text{or } 0.00436 \times 30 = 0.1308 \text{ gram } Na_2Cr_2O_7.$$

2. $5 \text{ cc. } \frac{N}{10} \text{ NaOH}, \quad 30 \text{ cc. } \frac{N}{10} \text{ Na}_2\text{S}_2\text{O}_3,$

$$\text{cc. } \frac{N}{10} \text{ NaOH} < \frac{1}{3} \text{ cc. } \frac{N}{10} \text{ Na}_2\text{S}_2\text{O}_3.$$

It has just been shown in case 3 that when bath is all $Na_2Cr_2O_7$ the cc. $\frac{N}{10}$ NaOH $= \frac{1}{3}$ cc. $\frac{N}{10}$ $Na_2S_2O_3$. Therefore, when the cc. $\frac{N}{10}$ NaOH $< \frac{1}{3}$ cc. $\frac{N}{10}$ $Na_2S_2O_3$ some of the chromium must be in the form of Na_2CrO_4, which does not react with NaOH and the bath is a mixture of Na_2CrO_4 and $Na_2Cr_2O_7$.

5 cc. $\frac{N}{10}$ NaOH reacts only with $Na_2Cr_2O_7$. Therefore,

$3 \times 5 = 15$ cc. $\frac{N}{10}$ $Na_2S_2O_3$ for $Na_2Cr_2O_7$.

Also, $30 - 15 = 15$ cc. $\frac{N}{10}$ $Na_2S_2O_3$ for Na_2CrO_4.

$$\frac{Na_2Cr_2O_7}{60{,}000} \times 15 = \text{grams } Na_2Cr_2O_7,$$

or $0.00436 \times 15 = 0.06540$ gram $Na_2Cr_2O_7$.

$$\frac{Na_2CrO_4}{30{,}000} \times 15 = \text{grams } Na_2CrO_4,$$

or $0.0054 \times 15 = 0.0810$ gram Na_2CrO_4.

5. 20 cc. $\frac{N}{10}$ NaOH, 30 cc. $\frac{N}{10}$ $Na_2S_2O_3$,

cc. $\frac{N}{10}$ NaOH $= \frac{2}{3}$ cc. $\frac{N}{10}$ $Na_2S_2O_3$,

$$Cr_2O_7^{=} + 6I^- + 14H^+ \rightarrow 2Cr^{+++} + 7H_2O + 3I_2,$$
$$H_2Cr_2O_7 + 4OH^- \rightarrow 2CrO_4^{=} + 3H_2O.$$

From the above we get:

$$H_2Cr_2O_7 = 6I = 6Na_2S_2O_3,$$
$$H_2Cr_2O_7 = 4NaOH.$$

Therefore, when the bath is all $H_2Cr_2O_7$, the cc. $\frac{N}{10}$ NaOH $=$ $\frac{2}{3}$ cc. $\frac{N}{10}$ $Na_2S_2O_3$.

$$\frac{H_2Cr_2O_7}{60{,}000} \times 30 = \text{grams } H_2Cr_2O_7,$$

$0.00366 \times 30 = 0.1098$ gram $H_2Cr_2O_7$.

4. 15 cc. $\frac{N}{10}$ NaOH, 30 cc. $\frac{N}{10}$ $Na_2S_2O_3$.

Since for $Na_2Cr_2O_7$ the cc. $\frac{N}{10}$ NaOH $= \frac{1}{3}$ cc. $\frac{N}{10}$ $Na_2S_2O_3$, and since for $H_2Cr_2O_7$ the cc. of $\frac{N}{10}$ NaOH $= \frac{2}{3}$ cc. $\frac{N}{10}$ $Na_2S_2O_3$, then when cc. $\frac{N}{10}$ NaOH $> \frac{1}{3} < \frac{2}{3}$ cc. $\frac{N}{10}$ $Na_2S_2O_3$ the bath contains some $Na_2Cr_2O_7$ and some $H_2Cr_2O_7$. This combination is difficult to calculate because both the $Na_2Cr_2O_7$ and the $H_2Cr_2O_7$ are represented in both the $\frac{N}{10}$ NaOH and

$\frac{N}{10}$ $Na_2S_2O_3$ reading.

Procter's calculations are as follows :

Let a = cc. $\frac{N}{10}$ $Na_2S_2O_3$ for $Na_2Cr_2O_7$ and $H_2Cr_2O_7$.

Let b = cc. $\frac{N}{10}$ $Na_2S_2O_3$ for $Na_2Cr_2O_7$.

Let c = cc. $\frac{N}{10}$ $Na_2S_2O_3$ for $H_2Cr_2O_7$.

(1) Then $b + c = a$.

Let a' = cc. $\frac{N}{10}$ NaOH for $Na_2Cr_2O_7$ and $H_2Cr_2O_7$.

Let b' = cc. $\frac{N}{10}$ NaOH for $Na_2Cr_2O_7$.

Let c' = cc. $\frac{N}{10}$ NaOH for $H_2Cr_2O_7$.

(2) Then $b' + c' = a'$.

(3) Also $b' = \frac{b}{3}$.

(4) And $c' = \frac{2c}{3}$.

Substituting (3) and (4) in (2)

$$\frac{b}{3} + \frac{2c}{3} = a', \text{ or}$$

(5) $b + 2c = 3a$.

(6) From (1) $b = a - c$.

Substituting (6) in (5) we get

$$a - c + 2c = 3a', \text{ or } a + c = 3a', \text{ or}$$

(7) $c = 3a' - a$,

but c = cc. $\frac{N}{10}$ $Na_2S_2O_3$ for $H_2Cr_2O_7$ and $c = 45 - 30 = 15$ cc. $\frac{N}{10}$ $Na_2S_2O_3$ for $H_2Cr_2O_7$.

$$\frac{H_2Cr_2O_7}{60{,}000} \times 15 = \text{grams } H_2Cr_2O_7,$$

$$0.00366 \times 15 = 0.0549 \text{ gram } H_2Cr_2O_7.$$

(8) $$a - c = b.$$

$$30 - 15 = 15 \text{ cc. } \frac{N}{10} \ Na_2Cr_2C_7,$$

$$\frac{Na_2Cr_2O_7}{60{,}000} \times 15 = \text{grams } Na_2Cr_2O_7,$$

$$0.00436 \times 15 = 0.0654 \text{ gram } Na_2Cr_2O_7.$$

Proposed Calculations.

If all chromium were in the form of $Na_2Cr_2O_7$, 10 cc. $\frac{N}{10}$ NaOH would have been used, but 15 cc. were actually used. Therefore, 15 cc. — 10 cc. = 5 cc. $\frac{N}{10}$ NaOH = 5 cc. $\frac{N}{10}$ H_2SO_4, which has changed some $Na_2Cr_2O_7$ to $H_2Cr_2O_7$.

$$Na_2Cr_2O_7 + H_2SO_4 \rightarrow H_2Cr_2O_7 + Na_2SO_4.$$

$$\frac{H_2Cr_2O_7}{20{,}000} \times 5 = \text{grams } H_2Cr_2O_7,$$

$$0.0110 \times 5 = 0.0550 \text{ gram } H_2Cr_2O_7.$$

10 cc. $\frac{N}{10}$ NaOH would be equivalent to the $Na_2Cr_2O_7$ if all chromium were in the form of $Na_2Cr_2O_7$, but an amount of $Na_2Cr_2O_7$ equivalent to 5 cc. $\frac{N}{10}$ H_2SO_4 has been changed to $H_2Cr_2O_7$.

Therefore, 10 — 5 = 5 cc. $\frac{N}{10}$ H_2SO_4 equivalent to the $Na_2Cr_2O_7$ remaining.

$$\frac{Na_2Cr_2O_7}{20{,}000} \times 5 = \text{grams } Na_2Cr_2O_7,$$

$$0.0131 \times 5 = 0.0655 \text{ gram } Na_2Cr_2O_7.$$

6. Since cc. $\frac{N}{10}$ NaOH $> \frac{2}{3}$ cc. $\frac{N}{10}$ $Na_2S_2O_3$, some free H_2SO_4 is present with the $H_2Cr_2O_7$.

The 30 cc. $\frac{N}{10}$ $Na_2S_2O_3$ is a measure only of the $H_2Cr_2O_7$.

$$0.00366 \times 30 = 0.10980 \text{ gram } H_2Cr_2O_7.$$

$$\frac{2}{3} \times 30 = 20 \text{ cc. } \frac{N}{10} \text{ NaOH for } H_2Cr_2O_7,$$

$$25 - 20 = 5 \text{ cc. } \frac{N}{10} \text{ NaOH for free } H_2SO_4.$$

$$\frac{H_2SO_4}{20,000} \times 5 = \text{grams } H_2SO_4,$$

$$0.0049 \times 5 = 0.0245 \text{ gram } H_2SO_4 \text{ present.}$$

RUTGERS COLLEGE,
NEW BRUNSWICK, N. J.

THE DETERMINATION OF FREE SULPHURIC ACID IN LEATHER. 1919 COMMITTEE REPORT.

By J. B. Churchill, Chairman, assisted by J. F. Anthes.

The quantitative estimation of free sulphuric acid or its equivalent in other mineral acids in leather has been for a long period of years a subject of considerable discussion among leather chemists. The problem is not one, however, that is peculiar to our leather industry; but is merely a specialized form of the perplexing question of the correct estimation of mineral acid in organic material, when such material may contain both organic and inorganic acids and their salts; also non-metallic elements such as sulphur and phosphorous in various complex combinations with the organic matter present. The commercial chemist has dealt with the problem in various ways; but no general method applicable to all classes of material has yet been found.

The determination of free mineral acid in leather presents about every imaginable difficulty, and up to the present time no one method has been found that could be applied to all classes of leather. It was the hope of the chairman that a general method for this determination covering all types of leather might be found, and that such a method after being worked out in a preliminary way in this laboratory, could be submitted for co-operative work to the Committee. After the expenditure of considerable time and effort, the conclusion was reached that the only method capable of giving reliable results is the much discussed method of Professor Procter, generally known as the Procter and Searle Method.

As the time available for this work was becoming limited, it seemed best that the Committee work for this year be confined to a further study of the work carried on by last year's Committee

under the direction of Mr. J. S. Rogers, (This JOURNAL 13, 319, 1918), and an attempt made to supplement, and in some degree complete the work of the 1918 Committee.

The recommendations of last year's Committee are as follows:

1. "It is recommended that a detailed study of the procedure of the Procter and Searle Method be made.
2. "That further study be conducted to determine the proper amount of alkali to use.
3. "That the effect of the alkalinity of the ash upon the acidity found be further investigated.
4. "That methods be developed for determining and correcting for materials such as Fe, Al, and NH_3 compounds.
5. "That any new methods giving promise of better results be reported."

The following work was outlined with the purpose of answering these and other questions presented in the discussion, as far as possible:

LABORATORIES AND PERSONNEL OF THE COMMITTEE.

Elk Tanning Co., Ridgway, Pa., G. W. Schultz.
Kistler, Lesh & Co., Morganton N. C., J. S. Rogers.
Graton & Knight Mfg. Co., Worcester, Mass., J. J. Meehan.
Leather & Paper Laboratory, Bureau of Chemistry, Washington, D. C., R. W. Frey.
Kistler Leather Co., Lock Haven, Pa., F. F. Marshall.
Bureau of Standards, Washington, D. C., L. M. Whitmore.
American Leather Research Laboratory, New York, N. Y., J. B. Churchill, Chairman, assisted by J. F. Anthes.

DIRECTIONS FOR COMMITTEE WORK ON THE DETERMINATION OF SULPHURIC ACID IN LEATHER.

Descriptions of Samples.

Sample A. This consists of vegetable-tanned sole leather before bleaching or stuffing.

Sample B. This consists of sample of vegetable-tanned sole leather bleached and loaded with both salts and glucose.

Samples C, D, E and F. These consists of four samples of commercial sole leather.

APPLYING TO SAMPLES A AND B.

1. Determine moisture and ash; using 5 grams.
2. Determine the alkalinity of the ash as follows:

To the ash residue add a known excess of tenth-normal sulphuric acid, heat on water bath for fifteen minutes. Wash into beaker and titrate with tenth-normal sodium carbonate using methyl orange as indicator. Report the result as minus acidity in terms of sulphuric acid.

3. On 2 grams of each leather determine the per cent. of free sulphuric acid using the following procedure: Two grams of the original leather are treated with 25 cc. of tenth-normal sodium carbonate, carefully evaporated to dryness, completely charred using as low a temperature as is possible. Add 25 cc. hot water and bring on filter collecting filtrate in 250 cc. beaker or flask. Wash filter and charcoal well with hot water. Ash filter and charcoal in original dish. Add 25 cc. tenth-normal sulphuric acid, heat on water bath for fifteen minutes. Wash through filter into dish containing first filtrate titrate using methyl orange as indicator.

4. To 2 grams of the original leathers A and B add such an amount of tenth-normal sulphuric acid as will exactly neutralize the alkalinity of the ash as found in No. 2. Evaporate to dryness on water bath, and determine the acidity by the Procter-Searle Method as given under No. 3.

5. Add to 2 grams of each of the original leathers such a volume of tenth-normal sulphuric acid as would correspond to the addition of 1 per cent. actual H_2SO_4. Evaporate to dryness and determine acidity as in No. 3.

6. As No. 5 but make determinations using 20 cc.-35 cc. and 50 cc. of tenth-normal sodium carbonate.

7. Repeat No. 5 and No. 6 with the exception that 3 per cent. of actual sulphuric acid is to be added.

APPLYING TO SAMPLES C, D, E AND F.

8. Determine the percentage of free sulphuric acid in samples C, D, E and F, using procedure as given under No. 3. If time permits repeat a number of these determinations using porcelain instead of platinum.

Note. The above determinations should be made in duplicate using platinum dishes for the ignitions.

The results of the Committee work are given in the following tables:

TABLE I.—RESULTS FOR No. 1 AND No. 2.

Analyst	Moisture		Total ash		Alkalinity of ash	
	Sample A	Sample B	Sample A	Sample B	Sample A	Sample B
G. W. Schultz	9.23	9.36	0.67	4.20	—0.53	—2.86
	9.98	10.38	0.65	4.18	—0.56	—2.72
Av.	9.60	9.87	0.66	4.19	—0.55	—2.79
J. S. Rogers	9.95	10.06	0.64	4.15	—0.51	—3.14
	9.91	10.09	0.69	4.07	—0.51	—3.12
Av.	9.93	10.08	0.67	4.11	—0.51	—3.13
J. J. Meehan	9.54	10.52	0.68	4.36	—0.54	—2.74
	9.82	10.20	0.76	4.44	—0.49	—2.57
	9.32	—	—	4.32	—	—
Av.	9.56	10.36	0.72	4.37	—0.52	—2.66
R. W. Frey	9.93	10.05	0.66	4.34	—0.55	—2.75
Av.	9.93	10.05	0.66	4.34	—0.55	—2.75
L. M. Whitmore	9.8	10.1	0.62	4.03	—0.52	—3.12
	9.7	10.0	0.61	4.02	—0.52	—3.20
	—	—	—	3.99	—	—3.16
Av.	9.8	10.1	0.62	4.01	—0.52	—3.16
F. F. Marshall	8.85	9.02	0.74	4.30	—0.63	—3.00
	8.89	9.05	0.69	4.20	—0.69	—3.16
Av.	8.87	9.04	0.72	4.25	—0.66	—3.08
J. F. Anthes	10.09	10.36	0.65	4.10	—0.50	—3.00
	10.17	10.52	0.63	4.20	—0.53	—3.10
Av.	10.13	10.44	0.64	4.15	—0.52	—3.05
Highest	10.17	10.52	0.76	4.44	—0.69	—3.20
Lowest	8.85	9.02	0.61	3.99	—0.49	—2.57
Average	9.66	9.99	0.67	4.19	—0.54	—2.97

TABLE II.—PROCTER AND SEARLE—Results for No. 3 and No. 8.

	Sample A		Sample B		Sample C		Sample D		Sample E		Sample F	
Analyst	Plat.	Porc.	Plat.	Porc.	Plat.	Porc.	Plat.	Porc.	Plat.	Porc.	Plat.	Porc.
G. W. Schultz	0.10		—0.17		0.49		—0.17		—0.15		—0.20	
	0.12		—0.17		0.59		—0.15		—0.12		—0.15	
Av.	0.11		—0.17		0.54		—0.16		—0.14		—0.18	
J. S. Rogers	0.07		—0.10			0.64		—0.07		—0.06		—0.12
	0.07		—0.12			0.69		—0.06		—0.06		—0.13
Av.	0.07		—0.11			0.67		—0.07		—0.06		—0.13
J. J. Meehan	—0.05		—0.12		0.57	0.67	—0.06	—0.06	—0.06	—0.09	—0.14	—0.23
	0.14		0.11		0.55		—0.05	—0.10	0.00	—0.06	—0.17	
	—0.12		—0.08					—0.07		—0.04		
Av.	—0.01		—0.03		0.56	0.67	—0.06	—0.08	—0.03	—0.04	—0.15	—0.23
R. W. Frey	0.17		0.15		0.66	0.65	0.09	0.11	0.25	0.23	0.00	0.00
Av.	0.17		0.15		0.66	0.65	0.09	0.11	0.25	0.23	0.00	0.00
L. M. Whitmore	0.12	0.16	—0.22	—0.14	0.67		—0.12	—0.24	0.12	0.16	—0.10	0.08
	0.14	0.22	—0.22	—0.12	0.70		—0.10	—0.10	0.08	0.38	—0.12	0.13
		0.14			0.67		—0.14			0.36		
					0.62					0.38		
					0.70							
Av.	0.13	0.17	—0.22	—0.13	0.67		—0.19	—0.17	0.15	0.32	—0.11	0.10

TABLE II.—(*Continued*)

Analyst	Sample A Plat.	Sample A Porc.	Sample B Plat.	Sample B Porc.	Sample C Plat.	Sample C Porc.	Sample D Plat.	Sample D Porc.	Sample E Plat.	Sample E Porc.	Sample F Plat.	Sample F Porc.
F. F. Marshall	0.10		0.00		0.49	0.73	0.08	0.12	0.00	0.00	0.15	0.25
	0.10		0.00			0.71		0.05		0.05		
						0.73		0.08		0.00		
Av.	0.10		0.00		0.49	0.72	0.08	0.08	0.00	0.02	0.15	0.25
J. F. Anthes	0.10		—0.10		0.55		—0.06		0.05		—0.20	
	0.13		—0.10		0.62		—0.10		0.06		—0.24	
	0.10		—0.11		0.60		—0.12		0.05		—0.22	
							—0.12		0.05		—0.20	
Av.	0.11		—0.10		0.59		—0.10		0.05		—0.20	
Highest	0.17	0.22	0.15	—0.12	0.70	0.73	0.09	0.12	0.25	0.38	0.15	0.25
Lowest	—0.05	0.14	—0.22	—0.14	0.49	0.64	—0.17	—0.24	—0.15	—0.09	—0.24	—0.23
Average	0.09	0.18	—0.07	—0.13	0.61	0.68	—0.08	—0.03	0.04	0.10	—0.10	0.02

TABLE III.—PROCTER AND SEARLE WITH ACID ADDED EQUIVALENT TO ALKALINITY OF ASH—Results for No. 4.

	Sample A				Sample B			
Analyst	Per cent. H_2SO_4 added	Per cent. found by P. & S.	Original acidity See Table II	Acid found Corrected for orig. acidity	Per cent. H_2SO_4 added	Per cent. found by P. & S.	Original Acid-ity	Acid found Corrected for orig. acidity
G. W. Schultz	0.53	0.56	0.10	0.49	2.86	2.33	—0.17	2.46
		0.61				2.25		
		Av. 0.59				Av. 2.29		
J. J. Meehan	0.52	0.63	—0.01	0.52	2.66	2.73	—0.03	2.41
		0.38				2.03		
		Av. 0.51				Av. 2.38		
R. W. Frey	0.55	Av. 0.75	0.17	0.58	2.75	Av. 2.70	0.15	2.55
F. F. Marshall	0.66	0.61	0.10	0.53	2.63	Av. 2.63	0.00	2.63
		0.64						
		Av. 0.63						
J. F. Anthes	0.52	0.58	0.11	0.47	3.05	2.65	—0.10	2.74
		0.57				2.62		
		Av. 0.58				Av. 2.64		

TABLE IV.—1 Per Cent. H_2SO_4 Added, with Varying Amounts of Na_2CO_3—Results for No. 5 and No. 6.

Analyst	20 cc N/10 Na_2CO_3 A	B	25 cc. N/10 Na_2CO_3 A	B	35 cc. N/10 Na_2CO_3 A	B	50 cc. N/10 Na_2CO_3 A	B
G. W. Schultz	1.08	0.88	1.03	0.69	1.20	0.96	1.42	1.23
	1.10	0.66	1.03	1.10	1.32	0.98	1.42	1.23
Av.	1.09	0.77	1.03	0.89	1.26	0.97	1.42	1.23
J. S. Rogers	1.02	0.86	0.96	0.99	1.03	0.87	0.83	0.91
	0.98	0.88	1.00	0.74	1.00	0.81	0.86	0.95
Av.	1.00	0.87	0.98	0.86	1.02	0.84	0.85	0.93
R. W. Frey	1.09	0.98	1.14	1.05	1.16	1.08	1.10	1.16
Av.	1.09	0.98	1.14	1.05	1.16	1.08	1.10	1.16
L. M. Whitmore	0.96	0.54	0.96	0.62	0.98	0.60	0.88	0.84
	0.92	0.56	0.98	0.68	0.92	0.64	0.84	0.84
	0.94	0.60	0.95					0.78
	0.98							1.00
Av.	0.95	0.57	0.97	0.65	0.95	0.62	0.86	0.89
F. F. Marshall	0.93		0.98	0.96	0.86		1.00	
Av.	0.93		0.98	0.96	0.86		1.00	
J. J. Meehan	1.15	0.83			1.22	0.91	1.21	0.87
	1.00	0.81			1.03	0.92	1.05	1.00
		0.62				1.12		1.15
								1.09
Av.	1.08	0.76			1.13	0.99	1.13	1.04
J. F. Anthes	0.96	0.70	0.98	0.81	1.20	0.88	1.30	1.05
	0.94	0.70	1.00	0.92	1.10	0.90	1.30	1.00
Av.	0.95	0.70	0.99	0.87	1.15	0.89	1.30	1.02
Highest	1.15	0.98	1.14	1.10	1.32	1.12	1.42	1.23
Lowest	0.92	0.54	0.95	0.62	0.86	0.62	0.83	0.78
Average	1.00	0.74	1.00	0.86	1.09	0.89	1.10	1.01

TABLE V.—3 Per Cent. H_2SO_4 Added with Varying Amounts of N/10 Na_2CO_3—Results for No. 7.

	3 per cent. N/10 H_2SO_4 20 cc. N/10 Na_2CO_3		3 per cent. N/10 H_2SO_4 25 cc. N/10 Na_2CO_3		3 per cent. N/10 H_2SO_4 35 cc. N/10 Na_2CO_3		3 per cent. N/10 H_2SO_4 50 cc. N/10 Na_2CO_3	
Analyst	A	B	A	B	A	B	A	B
G. W. Schultz	2.91	2.05	3.06	2.43	3.16	3.09	3.36	3.23
			3.11	2.43				
Av.	2.91	2.05	3.09	2.43	3.16	3.09	3.36	3.23
J. S. Rogers							2.90	
							3.07	
Av.							2.99	
J. J. Meehan	2.72	1.57			3.06	2.74	2.99	2.80
					2.93	2.74	3.00	2.86
Av.	2.72	1.57			2.99	2.74	2.99	2.83
R. W. Frey			3.19	2.91				
Av.			3.19	2.91				
L. M. Whitmore	3.00	1.43	3.00	2.27	3.00	2.77	2.98	2.88
	2.96	1.41	2.92	2.41	2.96	2.81	2.98	2.78
	2.98	1.39		2.20	2.97	2.81	2.96	2.81
						2.83		
						2.81		
Av.	2.98	1.41	2.96	2.29	2.31	2.81	2.97	2.82
F. F. Marshall	2.33		2.45	2.57	2.57		2.57	
Av.	2.33		2.45	2.57	2.57		2.57	
J. F. Anthes	2.98	2.05	3.14	2.40	3.20	3.01	3.21	3.33
			2.82	2.35	3.20	3.07		
			2.89					
Av.	2.98	2.05	2.94	2.38	3.20	3.04	3.21	3.33
Highest	3.00	2.05	3.19	2.91	3.20	3.09	3.36	3.33
Lowest	2.33	1.39	2.45	2.20	2.57	2.74	2.57	2.78
Average	2.84	1.65	2.95	2.44	3.01	2.87	3.00	2.96

Theoretical Discussion.

Before discussing the results themselves it may be well to consider for a moment the Procter and Searle Method from its theoretical side.

For the present purpose we can limit the discussion to the estimation of free mineral acid in vegetable-tanned leather as this method is not applicable to the mineral tannages.

The Procter and Searle Method depends on the addition of a known amount of Na_2CO_3 to a given weight of leather, ashing, and adding an exactly equivalent amount of acid, and titrating the excess of acid or alkali.

Taking into consideration the various factors which can influence this determination we have:

(1) Organic material; hide, tannin, organic acids, etc.

(2) Organic salts of calcium, magnesium and the alkalies.

(3) Calcium and magnesium as carbonates.

(4) Added magnesium sulphate (Epsom salts); also calcium sulphate, and other inorganic salts of calcium, magnesium, and the alkalies.

(5) Sulphur in organic combination with the hide, and as introduced by the use of sulphonated oil, bisulphited extract, sulphite cellulose or in the form of a sulphonic acid introduced by the use of the newer synthetic tanning materials.

(6) Actual free sulphuric acid present or its equivalent in other mineral acid.

If mineral acid be added to a leather which contains organic salts of the alkalies or alkaline earths, an interchange will take place; an equivalent amount of the organic acid being set free if sufficient organic salts be present. If the acid be in excess, the amount will be reduced exactly in proportion to the amount of salts of this nature that are present. Should such salts be in excess, the leather will give an alkaline reaction with the Procter and Searle, as all these compounds are reduced to the carbonates or oxides of the alkalies or alkaline earths on ignition.

If a leather contains, which is perhaps unlikely, any calcium or magnesium as the carbonate or oxide, the amount of acid will be reduced in the proportion that these substances are present.

The mineral salts that influence this determination are first, magnesium sulphate which may be present in amounts up to 7 or

8 per cent. sodium sulphate originally present, or formed by the addition of the sodium carbonate, and in a lesser degree calcium sulphate originally present in the leather. For any discussion of the correct amounts of alkali to add or the effect of alkalinity of the ash, it is necessary to know the behavior of these salts when ignited alone, and when ignited in the presence of organic material.

Magnesium Sulphate (epsom salts).

When ignited at a medium red heat, magnesium sulphate shows but little, if any decomposition. At higher temperatures it loses acid. and becomes converted into a mixture of the oxide and sulphide (O. Dammer, *Handbuch der Anorganischen Chemie* 11^2, 426). When burned in the presence of organic material, hydrogen or hydrocarbons, it is converted into the oxide, MgO, with loss of S. and H_2S. No magnesium sulphide can be produced (Daubeny, Edinb, Phil. J. 7-111; Baussingault, A. ch. (4) 12-419; Unger, A. 81-830;) Ignited with carbon, or in presence of CO it is converted into the oxide without the production of the sulphide. (Gay Lussac, J. pr. 11-68; Stammer, J. pr. (2) 12-65, Jacquemin, C. r. 46-1164; J.-1858-86.)

Sodium Sulphate.

This salt when ignited alone shows but little decomposition except at high temperatures. Ignited with carbon or organic material in sufficient quantity, it is quantitatively converted to the sulphide. This on oxidation is reconverted without loss of sulphur to the original sulphate. (Unger, A. 63, 240; Scheurer-Kestner, A. ch. (4) 1-412; Mactear, B. 11-1696; O. Dammer, *Handbuch der Anorganischen Chemie* 11^2 160.)

Calcium Sulphate.

When ignited alone, calcium sulphate, melts at a red heat without decomposition. At a white heat it loses some of its SO_3. (O. Dammer, *Handbuch der Anorganischen Chemie* 11^2 315; Mitscherlich, J. pr. 83-485; Bunsen, A. 111, 456; Boussingault, A. ch. (4) 12-419.) When burned with carbon or organic matter it is quantitatively reduced to the sulphide. (Berthier, A. ch. 22-233.)

CaS on oxidation at a red heat is completely reconverted to $CaSO_4$. Unger, *loc. cit.;* O. Dammer, *Handbuch der Anorganischen Chemie* 11^2 310).

The influence of other salts than those described is small. Sodium chloride has no appreciable effect on the determination. Magnesium and calcium chlorides will have no effect providing sufficient sodium carbonate is added to accomplish their decomposition.

If sulphur is introduced into the leather in any of the forms above stated it will increase the apparent acidity unless the material used contains enough base to neutralize its effect. Each case would have to be studied as a special problem. The sulphur naturally combined with the hide may to some extent, increase the acidity found by the Procter and Searle Method. It would be converted by ignition in the presence of Na_2CO_3 into the sulphide which would in turn oxidize to the sulphate thereby causing a loss of sodium carbonate.

From the above facts we can determine the conditions under which the Procter and Searle determination should be run, and make the following general statements regarding this determination.

1. Ignition should be as complete as possible before filtering takes place. Every chance should be given for the reoxidation of any sodium sulphide formed.

2. The amount of sodium carbonate added should be sufficient not only to combine with any free acid that may be present; but to completely decompose whatever magnesium sulphate may exist in the leather.

3. Digestion of ash with the added acid should be carried out in such a manner that a complete reaction is obtained. Boiling or heating on the water bath for at least a fifteen minute period is necessary to good results.

4. The alkalinity of the ash has no relation to the amount of acid present in the leather or the amount of acid found by the Procter and Searle determination.

Discussion of Experimental Results.

In Table I the results on moisture, total ash and alkalinity of the ash are given. There is practically no discussion on these results, since the figures of the Committee agree as closely as might be expected. There is a maximum variation of 0.15 per cent. for the total ash in Sample A. and of 0.45 per cent. for total

ash in Sample B. The alkalinity of the ash shows a maximum variation of 0.20 per cent. for Sample A, and of 0.63 per cent. for Sample B. This larger variation that is noted for Sample B is in accordance with what might be expected from the behavior of magnesium sulphate when ignited in the presence of organic matter.

Table II gives the results of the Committee for the acidity of all six leathers as found by the Procter and Searle Method, using 25 cc. of Na_2CO_3. The maximum variation found by different operators is as follows:

Sample	Per cent.
A	0.22
B	0.37
C	0.21
D	0.26
E	0.40
F	0.39
Average	0.31

The variation from the average is:

Sample	Per cent.
A	0.14
B	0.22
C	0.12
D	0.17
E	0.21
F	0.25

The above figures show that, with careful work the Procter and Searle Method will give results accurate to within 0.2 to 0.3 per cent. of the actual amount of sulphuric acid present, based on the weight of the original leather.

Table III gives the Committee's results for the acidity of leathers A and B as determined by the Procter and Searle Method, after an amount of acid had been added exactly equal to the alkalinity of the ash. For leather A, the amount of free acid found was practically equal to that which had been added. For leather B, the amount of acid found, after correcting for the original acidity, was slightly lower than the amount added.

The average amount of acid added to correct for the original alkalinity for Sample B was 2.79 per cent. while that found, after

correcting for original acidity was 2.56 per cent. These figures very clearly show that no relation exists between the alkalinity of the ash and the amount of acid, as found by the Procter and Searle Method.

Tables IV and V give the Committee results for leathers A and B when 1 and 3 per cent. of sulphuric acid had been added respectively to the original leathers, and run in each case with 20, 25, 35 and 50 cc. of sodium carbonate.

Taking the average acidity for samples A and B as determined in Table II the per cent. of acid found should be 1.09 per cent. and 3.09 per cent. for Sample A, and 0.93 and 2.93 per cent. for Sample B. The average results found by the Committee are given in the following table:

1 Per Cent. H_2SO_4 Added.

Cc. Na_2CO_3 added	Sample A	Sample B
20	1.00	0.74
25	1.00	0.86
35	1.09	0.89
50	1.10	1.01

3 Per Cent. H_2SO_4 Added.

Cc. Na_2CO_3 added	Sample A	Sample B
20	2.84	1.65
25	2.95	2.44
35	3.01	2.87
50	3.00	2.96

In the case of Sample A, the results obtained using different amounts of sodium carbonate, agree as closely as could possibly be expected with the theoretical.

Regarding Sample B, however, it will be noted that there is considerable variation in the results obtained. The use of increasing amounts of sodium carbonate yields an increasing percentage of acid, which with 35 and 50 cc. of sodium carbonate coincides very closely with the theoretical figures, namely, 0.93 per cent. and 2.93 per cent.

In order to discuss the question of the correct amount of alkali to add, and to confirm the theoretical statements made in an earlier part of this paper the following experimental work was carried out.

Effect of Magnesium Sulphate (Epsom Salts).

A sample of magnesium sulphate, Merck's C. P. crystalized, was ground to fine powder to insure uniformity of sample. One gram portions were ignited in platinum, first at a low temperature, and then at a bright red heat. The per cent. of residue and its alkalinity was then determined.

$MgSO_47H_2O$ Weight taken	Residue Per cent.	Alkalinity of residue as minus H_2SO_4 Per cent.
1.0000	46.10	3.50
1.0000	46.20	3.43
1.0000	44.80	4.10
1.0000	45.48	3.82
1.0000	45.45	3.82

One gram of magnesium sulphate prepared as above, was added to 10 grams of tanned hide powder, and ignited in platinum under the same conditions. The weight of ash from 10 grams of tanned hide, was 0.0245 gram. This ash required 3.4 cc. N/10 H_2SO_4 for neutralization. The results are given in the following table:

I. Weight of ash 10 grams tanned hide and 1 gram $MgSO_47H_2O$	II. Weight of ash 10 grams tanned hide	III. Weight of ash of $MgSO_47H_2O$ Corrected for II.
0.2051	0.0245	0.1806
0.2038	0.0245	0.1793
0.2035	0.0245	0.1790
0.2038	0.0245	0.1793
0.2046	0.0245	0.1801

IV. Alkalinity of residue 10 grams tanned hide and 1 gram $MgSO_47H_2O$ cc. N/10 H_2SO_4	V. Alkalinity of residue 10 grams tanned hide cc. N/10 H_2SO_4	VI. Alkalinity of ash from $MgSO_47H_2O$ Corrected for V. Per cent.
47.2	3.40	21.46
47.3	3.40	21.50
47.3	3.40	21.50
47.2	3.40	21.46
47.2	3.40	21.46

This experiment was repeated using Sample A in place of tanned hide powder. The alkalinity of 1 gram of magnesium sulphate ignited under these conditions and corrected for the alkalinity of the ash from the 10 grams of leather, was found to be 13.32, 13.42, and 13.50 per cent. This is in accordance with what

might be expected, leather A, having a higher ash than the tanned hide powder, so that a portion of the acid freed from the magnesium sulphate during ignition, would be held back by the greater amount of alkali present.

To further show the effect of magnesium sulphate on the alkalinity of ash, various amounts were added to leather A. The leather was ashed as usual, and the alkalinity determined.

Leather A

$MgSO_4 7H_2O$ added per cent.	Alkalinity of ash as minus H_2SO_4
0.00	0.54
2.00	1.20
5.00	2.16
10.00	3.80

EFFECT OF SODIUM SULPHATE ON ALKALINITY OF ASH.

To show the effect of sodium sulphate the following experiments were made: To 2 grams of Sample A, 0.1000 gram (5 per cent.) of Na_2SO_4 was added. The sample was burned, and the alkalinity of ash was determined in the usual manner. The results are as follows:

	Per cent.
I	0.59
II	0.58
III	0.54
Av.	0.56

This shows but little change from the original alkalinity of 0.54 per cent. expressed as minus sulphuric acid.

EFFECT OF SODIUM SULPHATE ON ACIDITY AS FOUND BY THE PROCTER AND SEARLE METHOD.

To 2 grams of Sample A, 0.1000 gram (5 per cent.) of Na_2SO_4 was added. The acidity was then determined by the Procter and Searle Method using 25 cc. N/10 Na_2CO_3 with the following results.

	Per cent.
I	0.12
II	0.12
III	0.12
IV	0.12
Av.	0.12

This result is the same as the 0.11 per cent. found by us for this leather.

THE EFFECT OF THE PRESENCE OF MAGNESIUM SULPHATE ON THE AMOUNT OF SODIUM CARBONATE NECESSARY TO BE ADDED IN THE PROCTER AND SEARLE DETERMINATION.

The above experiments clearly show that magnesium sulphate is decomposed when burned with leather while sodium sulphate has little if any effect on the determination.

In an earlier part of this paper the statement has been made that a sufficient amount of sodium carbonate must be present to both neutralize any free acid which may be present, and to completely decompose the magnesium sulphate existing in the leather. To more conclusively emphasize this point the following experiments were carried out.

The amount of $MgSO_47H_2O$ in Sample B, was carefully determined. This was found to be 7.74 per cent. and 7.76 per cent. as the result of two determinations or an average of 7.75 per cent. $MgSO_47H_2O$. The amount of Na_2CO_3 necessary to decompose the $MgSO_47H_2O$ in 2 grams of leather was found to be 0.0667 gram which is equivalent to 12.57 cc. N/10 Na_2CO_3.

As the leather was practically neutral no account was taken of the acidity. The above amount of alkali was added to the leather, which was then ashed, and the alkalinity determined as usual. The alkalinity of the ash found after correcting for the 12.57 cc. of Na_2CO_3 introduced was found to be 0.29 per cent., 0.28 per cent. and 0.29 per cent. respectively, as a result of three separate determinations, expressed as minus sulphuric acid.

A further experiment was conducted in which 6.5 cc. of N/10 Na_2CO_3 were added to 2 grams of Sample B, which was then ashed and its alkalinity determined. In this case the alkalinity of the ash after correcting for the alkali added, was found to be 1.67 per cent., 1.64 per cent., 1.63 per cent. expressed as minus sulphuric acid.

Referring again to Tables IV and V giving the results of the Committee work, the following statements may be made relative to these results: It will be noted that for Sample A, the results are in very close agreement with the amount of acid that should have been obtained. Sample B, was found to contain 7.75 per cent. $MgSO_47H_2O$. The amount of Na_2CO_3 necessary to decompose this for a 2-gram sample would be 12.6 cc. of N/10 Na_2CO_3. For 1 per cent. added acid, the amount of Na_2CO_3

required would be 4.08 cc. making a total of 16.68 cc. N/10 Na_2CO_3 for the 2-gram sample. It is, therefore, evident that 20 cc. N/10 Na_2CO_3 should be sufficient. It is difficult to draw any conclusion since six of the thirteen results obtained are within the range of experimental error, while the balance show a lower figure than should be found. When 25, 35, or 50 cc. of N/10 Na_2CO_3 were used the average results found agree very closely with the theoretical.

When 3 per cent. of acid was added the amount of N/10 Na_2CO_3 required by theory should have been 12.24 cc. to neutralize the 3 per cent. of acid and 12.6 cc. to decompose the $MgSO_4$-$7H_2O$ present. Hence a total of about 24.84 cc. N/10 Na_2CO_3 should have been required.

Abviously 20 cc. N/10 Na_2CO_3 would give low results, and this is borne out by the data obtained and found in Table V. Twenty-five cubic centimeters would be barely sufficient, and here a tendency towards low results is found. With 35 and 50 cc of N/10 Na_2CO_3 the results are in close agreement with the theory.

Effect of Added Acid on Alkalinity of Ash.

Various amounts of acid were added to Samples A and B, the leathers were then burned without the addition of Na_2CO_3, and the alkalinity of the ash determined as minus sulphuric acid. The results are given in the following table:

Analyst	Per cent. H_2SO_4 added	Alkalinity of ash Expressed as minus H_2SO_4	
		Sample A	Sample B
J. J. Meehan	1	0.38	1.62
	3	0.27	0.88
J. F. Anthes	1	0.40	2.57
	3	0.37	2.25
	5		1.54
	10		1.18

While no conclusion can be drawn from the above figures as regards the effect of the alkalinity of the ash on the amount of acid that would be found by the Procter and Searle Method, it is interesting to note that both of these leathers give an alkaline ash, no matter how large an excess of acid was added.

Digestion of the Ash With Acid Before Titration.

It has been the experience in this laboratory that a considerable error may be introduced into this determination if the ash

left from the ignitions with the Na_2CO_3 is not properly digested into the excess of acid added. This point was very clearly brought out by G. W. Schultz in last year's Committee Report.

Chairman's Conclusions and Recommendations.

In conclusion the chairman would make the following comments regarding the Procter and Searle Method for the determination of free mineral acid in leather.

1. *Ignition*—It would seem to matter but little, whether the burning takes place slowly or rapidly. The burning should be as complete as possible before filtering in order to allow complete oxidation of any sulphides that may have been produced by reduction of sulphates.

The amount of alkali added should be somewhat in excess of that required to neutralize the actual acid present, and to completely decompose into the corresponding carbonate any magnesium sulphate present in the leather. It would be the Chairman's recommendation that for a loaded leather 35 or 50 cc. of N/10 sodium carbonate be added for a 2-gram sample.

The Chairman would make the following recommendations regarding the procedure to be followed in carrying out the determination by the Procter and Searle Method with a vegetable-tanned leather. To a 2-gram sample, add 25 cc. of N/10 sodium carbonate in the case of an unloaded leather or a larger amount, 35 or 50 cc. in the case of a leather highly loaded with Epsom salts. After careful evaporation to dryness, ignite the contents of the dish until as much of the carbon is burned off as possible. Add 25 cc. of hot water, and digest a few moments. Filter the solution into a 300 cc. flask. Wash the filter paper and unburned carbon well with hot water, and return to the dish and completely ignite. To the remaining ash, add an amount of N/10 sulphuric acid equivalent to the amount of sodium carbonate used, and digest for at least fifteen minutes either on the water bath or on a hot plate. Filter into the flask containing the first filtrate, and titrate the excess of acid with N/10 sodium carbonate using methyl orange as the indicator.

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ABSTRACTS.

The Synthesis of Tannin and Similar Substances. E. Fischer and M. Bergmann, *Ber.*, (1918), 51, 1760; *J. S. D. and Col.*, 35, 77, (1919). The frequently expressed opinion that the so-called "Chinese tannin" contains a pentadigalloylglucose as the essential constituent has hitherto lacked experimental proof; the synthesis of such a compound from glucose and digallic acid failed owing to the unfavorable properties of the carbomethoxy compounds (*Ber.* 1913, 46, p. 3280). Recently the pentacetyl derivatives of meta and para-digallic acids and the corresponding chlorides have been obtained as well as crystalline and easily purified compounds (*Ber.*, 1918, 57, p. 45). These chlorides have now been condensed with α and β-glucose in presence of quinoline. The products, although amorphous, are undoubtedly penta-(pentacetyl-digalloyl)-glucoses. The corresponding pentadigalloyl glucoses were obtained by careful hydrolysis with caustic soda in aqueous acetone solution at 0° C. The products obtained in this manner were typical tannins.

Penta-*m*-(digalloyl)-β-glucose is, in its solubility, in the general properties of tannins, in the reaction with arsenic acid solution, and in its specific rotation in organic solvents, remarkably similar to Chinese tannin (gall nuts?). Both products, on complete hydrolysis, give approximately equal quantities of glucose and gallic acid respectively. The only appreciable difference shown is in the specific rotation in aqueous solution. This solitary difference between the synthetic and natural products is not regarded as being of fundamental importance by the authors, on account of the fact that, when solutions are colloidal it is well known that small factors greatly influence optical activity.

Leathers From Aquatic Animals. *Commerce Reports.* The Bureau of Fisheries has received from the Ocean Leather Co., of New York, a sample lot of leathers made from the skins of various aquatic animals, including ray, shark, sturgeon, paddlefish, and porpoise. It has received also articles made from such leathers, including men's, women's, and children's shoes, as well as a belt, wallet, portfolio, brief case, etc. This company has established stations on the South Atlantic and Gulf coasts where supplies of raw material are obtained, and is producing from such sources a very high grade of leather suitable for nearly every purpose for which leather is used.

The Properties and Uses of Some Titanium Compounds. By Joseph Barnes, *J. Soc. Dyers and Col.*, 35, 59 (1919). Titanium sodium sulphate, the most important of the commercial salts of titanium is a white powdery substance and is difficultly soluble in pure water. Boiling water at once decomposes it, giving rise to the formation of insoluble and inert meta-titanic acid. By adding a certain amount of acid, *e. g.*, sulphuric or oxalic, it may readily be dissolved by heating. A strong solution may be obtained by stirring it with cold water for a long time; one part of the salt mixed with two or three parts of cold water and stirred fre-

quently for several days will yield a liquor of high specific gravity which may be diluted down to a certain point without suffering decomposition. When highly diluted, the titanium hydroxide—titanic acid—is mostly thrown down. This decomposition may be prevented by adding an acid to the diluting water. The strong liquor may be neutralized to a great extent by the addition of an alkali, and it is possible to obtain an extremely basic product which remains in solution so long as it is kept cold and concentrated, but when diluted even to a moderate extent the bulk of the titanium is thrown down as hydroxide. Heating will, of course, quickly convert the precipitate into meta-titanic acid. It is noteworthy that this meta form of titanium hydroxide is practically useless for tinctorial purposes, and the dyer should always be on the alert with regard to the failures arising from its accidental formation. All unnecessary heating and dilution should be avoided. By adding a certain amount of sulphuric acid, however, a highly diluted solution of the sulphate may be heated up to 40° C. without suffering material change, and in this way it has been made possible to use the titanium sulphate in place of the more expensive oxalate compounds in the dyeing of leather.

An excellent way of obtaining a solution of titanium sodium sulphate is as follows: One part of the salt is mixed with nine parts of a cold solution of Glauber's salt of 5° Twaddell and by stirring the mixture from time to time for several days a stable solution will be obtained with only a trifling amount of residue, and will contain about 2 per cent. of TiO_2. It will keep in the cold almost indefinitely and may be diluted with a considerable amount of cold water. If instead of diluting with pure water a solution of Glauber's salt of 2° Twaddell be used, the dilution may be carried to almost any extent. A liquor prepared in this manner serves as a most suitable fixing bath for tanned yarn or cloth; the sodium sulphate not only increases the stability of the bath, but retards the transfusion of tannic acid into the fixing liquor.

Titanium Potassium Oxalate is produced commercially in a very pure form, and was, until the high price of potash rendered its economical manufacture an impossibility, extensively used by leather dyers. It yields very stable solutions which may readily be obtained by the assistance of heat. A sodium oxalate compound has been put on the market under the name of "Titox," which replaces quite satisfactory the, at present, expensive potash salt. It does not dissolve quite so quickly, but if one or two very simple precautions are taken a solution may be obtained which will answer just as well as the potash salt. It may be mentioned here, with regard to the use of these oxalates in leather dyeing, that the hardness of the water may have a disturbing effect. Hard water should be corrected by adding to it sufficient oxalic acid to convert the whole of the calcium, whether it be in the form of carbonate or sulphate, into calcium oxalate.

The titanium ammonium oxalate is much more soluble in cold water than the potassium compound, and is, therefore, not so readily obtained free from iron. Titanium-tanno-oxalate is simply a solution of tannate

of titanium in oxalic acid. The difficulty of obtaining titanium compounds free from iron increases largely the cost in the manufacture of pure titanium salts. Where iron does not interfere, or where it may even be an advantage, it is possible to make use of a cheap material. Such a material has recently been introduced. Iron tannate, as before mentioned, is more sensitive to the action of acids than is the case with titanium tannate, and by varying the degree of neutralization of the iron-titanium liquor, every shade of brown intermediate between buff and greyish-blue may be obtained by very simple operations. As an example of the process, the following may be given: The cloth or yarn is first tanned in the ordinary way. It is then passed into a liquor prepared as follows: 70 cc. of the strong liquor having a specific gravity of 1.400 is partially neutralized with a solution of soda ash containing 17 grams of Na_2CO_3. Then add 450 cc. of a solution of Glauber's salt of 5° Twaddell and dilute the whole down to 1 liter with cold water. The cloth or yarn is then squeezed or wrung up, allowed to lie off for about a quarter of an hour, and then washed. By putting the dyed material through these operations a second or third time, any depth of shade may readily be obtained. For pale shades the strength of the tannin bath may be reduced, but it is not advisable to reduce the strength of the titanium bath. Brighter and rather redder shades of brown are got by finishing off in a warm tannin bath. It is needless to say that material treated in this manner may at once be dyed up with any basic color. It may also be dyed up with the alizarins, although the tannic acid in combination with the titanium and iron may retard more or less the absorption of the color, and it is better, therefore, to pass the cloth before dyeing with Alizarin through a warm alkaline dunging bath, which may consist simply of water containing 1 or 2 grams of Na_2CO_3 per liter.

The Tanning Industry of Madras. (From the report of the Director of Industries, of Madras, furnished by the American Consul. Received through the courtesy of The Tanners Council of the U. S. A.) Owing to the demands of the war office for tanned hides and of the military departments in India, for leather accoutrements of all descriptions, the tanning and leather industries of the Presidency enjoyed a period of great prosperity. Owing to the need of conserving supplies of bark for the tannage of hides, it was not possible to relax the prohibition of the tanning of skins, and this branch of the industry remained in abeyance. But the demands of the war office for hides were inexhaustible, and many of the skin tanners were able to use their tanneries for the tanning of hides. At least three-fifths of the upper leather used in the united kingdom in the manufacture of boots for the British and Allied armies are supplied from the rough-tanned cow hides, known as East India tanned kips, from the Madras and Bombay tanneries and the magnitude of the trade may be estimated from the fact that the requirements of army upper leather for the year 1917 were estimated at 80,000,000 feet. In August, 1916, the Indian Government at the request of the war office

assumed complete control of the trade, and the whole of the available supply of East India tanned kips was purchased for export direct to the war office. On the creation of the Indian Munitions Board in February, 1917, the control of the arrangements for the purchase of kips was taken over by the board. A large increase of production has been one result of this control, but the action taken by the Indian Munitions Board has not been confined merely to increasing production. Efforts have been made to increase the proportion of army selection leather and to reduce the proportion of light weights and rejections which, although they command a high price at home, are unsuitable for army work. With this object in view the scale of prices has been so arranged as to offer greater profits to tanners who purchase the best selections of hides than to those who tan merely average lots. Steps have also been taken to prevent adulteration and undue weighing of hides. In the early days of the Government scheme it was found that the practice of adulterating hides by adding, in the process of tannage, magnesium salts, sugar and other adulterants was on the increase, and eventually with the full approval of the business firms in Madras adulteration was made a penal offense by an order passed under the Defence of India Rules. Another pernicious practice, that of improper greasing was also put a stop to by action under the Defence of India Rules. The object of greasing is mainly to add to the weight of the hide and to conceal cuts and other defects by the application after tannage of chalk and plaster to the flesh side. It is not injurious to the leather in the same way as adulteration and some people think that provided that it is not applied in excess, grease has some value of preservation. But in the main it is merely a form of artificial weighting. The result of the measures taken has been a remarkable improvement in the East India kips produced in the Madras tanneries, and it has been found possible also to simplify the classification of Madras tannages. All tannages are now classified in the four main grades—primes, best, good and ordinary, each of the first three being subdivided into two classes according to their growth and spread. It is a most important question whether the improvement thus effected in Madras kips cannot be made permanent. In present circumstances the question is comparatively simple since not only have Government extraordinary power under the Defence of India Rules but also being the only buyer, they are in a position to impose their wishes on the tanners. When after the war, trade resumes its normal course, the question will become much more difficult.

The immense demand of the war office for tanned hides and the increase of production resulting from this demand and from the measures taken by the Indian Munitions Board brought into great prominence the question of supplies of tanning barks. Madras owes its prominent position in the Indian tanning industry mainly to the fact that the Presidency is prolific in *Cassia auriculata* known as Avaram in Madras, and in the rest of India as Tarwad. The bark of this shrub is the great tanning material of Southern India. Its merits are that it is very easy

to use and quick in its action, it adds weight and plumpness to the hides and produces a leather which is capable, after further treatment by the currier, of being turned to a variety of uses. The price of avaram rose very high owing to the demand for the bark, and the question became so pressing that eventually control was taken over supplies.

Avaram bark will always remain the most important tanning material of the Madras presidency and the future of the tanning industry will always be bound up intimately with the question of cheap and plentiful supplies of the bark. This question has been brought to the notice of the Government, and measures have been taken to encourage the growth of the shrub. But the question of substitutes has also come into prominence. It is being dealt with at the factory of the Esociet Company at Maihar which has been acquired by the Indian Munitions Board, but useful work has also been done on new tanstuffs and mixtures at the Leather Trade School at Washermanpet.

With the object of meeting the increased demand for tanning materials, the Indian Munitions Board imported a consignment of black wattle bark from South Africa, but it was considered unadvisable to distribute the bark broadcast to tanners until careful experiments had been made and these experiments were conducted at the Leather Trade School by Mr. Kurup under the supervision of Captain Guthrie. Two sets of experiments were tried, some with wattle bark alone and others with mixtures of avaram and wattle in different proportions. Wattle bark is now being used in quite a number of tanneries. It can also be used with Konnai (*Cassia fistula*) bark.

	Sample 1 (much red leaf)	Sample 2 (a bright green sumac)
Tannin absorbed by chromed hide powder	33.14	24.99
Soluble non-tannin	16.11	14.98
Insoluble matter	50.75	60.03
Moisture	00.00	00.00
Total	100.00	100.00

A sample purely composed of red (young) leaves gave the following results:

Tannins absorbed by chromed hide powder	49.21
Soluble non-tannin	14.02
Insoluble matter	36.77
	100.00

Mr. Pilgrim, the tannin expert to the Government of India, whose headquarters are at Maihar, was invited by Government to visit the Madras presidency in order to investigate the resources of the presidency in tanning materials, and with the permission of the Indian

Munitions Board, he spent some weeks in the presidency in September last. It was agreed that he should investigate chiefly *Anogeissus latifolia,* the wattles and the mangroves of the Presidency. Mangroves were studied in the Tanjore district and in the back waters of Travancore. The mangrove swamps of Tanjore are well known, but unfortunately they consist almost entirely of *Avicennia Officinalis* which contains very little tannin. In Travancore the mangrove has, in recent years, been displaced very largely by the cocoanut, but one swamp was discovered where *Sonneratias, Bruguieras,* and *Rhizophoras* were common. All these mangroves are rich in tannin. *Anogeissus latifolia* was studied on the Kodaikanal ghat where a flush of young leaves was on. Bulk samples both of young and large leaves were powdered into sumacs and gave the preceding analyses:

It will be seen that the young leaves are very rich in tanning content, and very promising results have also been obtained at the Leather Trade School with twig bark. The tree is abundant in Tinnevelly, Madura, North Arcot, Salem, Anantapur, Bellary and Kurnool, and there should be a great future before this tanstuff not only for use in Southern India but also quite possibly, for export. All three species of the wattles (*Acacia decurrens, dealbata, and melanoxylon*) are common on the Nilgiris and on the Palnis. The leaves contain tannin but the bark, especially of *Acacia decurrens,* the common wattle, is rich in tannin content. The tannin content has been found by Hooper to be 25 per cent. in the upper stem bark; 33 per cent. in the lower stem bark and only 15 per cent. in the branch bark, but it has still to be decided by experiment whether better leather is produced by the stem bark or the twig bark, and experiments are to be made at Maihar to decide this point. Wattle bark from the Nilgiris and the Palnis should prove a useful supplement to avaram which will probably always remain the mainstay of the Madras tanners. Mr. Pilgrim examined the wattle forests of the Palnis and found them to consist mainly of *Acacia decurrens.* Information supplied by Mr. P. M. Lushington, Conservator of Forests, Southern Circle, and the District Forest Officer of the Nilgiris, however, indicated that the quantities of bark available, both on the Palnis and on the Nilgiris were not likely to exceed 200 tons a month. Extensive plantations would be necessary before an extract factory would become a commercial proposition. This question, however, has already attracted the attention of private enterprise.

On Mr. Pilgrim's advice Mr. Rajamanikkam Navadu was deputed to Maihar to study the "porridge" method of tanning, the object of which is to extract more completely the tannin in the tan stuff used. With the methods now in use in Madras, it may be noted, 7 per cent. of tannin remains in the spent bark which is thrown away. A programme of mixture and other experiments was also drawn up with Mr. Pilgrim's help, and these experiments went on continuously at the Leather Trade School throughout the latter part of the year. The first series consisted of thirty preliminary experiments on sheepskins with new tanstuffs either by themselves or in different mixtures. The new tanstuffs tried were

Anogeissus latifolia red sumac, *Anogeissus latifolia* green sumac *Anogeissus latifolia* twig bark, *Carissa spinarum, Xylia dolabriformis, Phyllanthus polyphyllus and Zizyphus xylopyra.* Twelve experiments were tried on hides. They were not completed by the end of the year and were carried on through the vacation. The results belong properly, therefore, to the report for the current year, but it may be mentioned that particularly promising results have been obtained from the twig and trunk bark of *Anogeissus latifolia,* so much so that the controller of tan stuffs has already felt justified in arranging for the exploitation of this bark in large quantities by the forest department for distributions through the Government depots to tanners. Printed vernacular instructions how to use the bark have also been issued. The bark of *Acacia decurrens* is also being freely issued to tanners for use with avaram, and so far every tanner who has used it has used it successfully. Red and green sumacs made from *Anogeissus* leaves are so strong that they cannot safely be issued at present to Indian tanners, but European tanners are ordering it in quantities and appear to find it satisfactory. Further large scale experiments are being carried on at the school with Gottihar fruit (*Zizyphus Xylopyra*) *Anogeissus latifolia* and *carissa spinarum.*

The Tanners' Council Meeting. Extracts from the *Shoe and Leather Reporter* for April 10, 1919. In one respect the meetings of the Tanners' Council in Boston on April 3 and 4 were the most important in the history of the industry. The question debated and answered was whether the Council should disband and the trade return to the former little more than social organizations which existed before the war.

The system of groups or divisions of tanners to consider their special and peculiar problems has worked well, and it would be a calamity if the progress made should be sacrificed, and the industry be permitted to slump back into its former condition of inertia and unpreparedness for emergencies.

There was some little objection to the continuance of the Council because of the expense. The budget for the coming year calls for an expenditure of nearly $88,000. This looks like a large amount of money until it is shown that it is an almost infinitesimal fraction of 1 per cent. of the annual leather business, as measured in dollars.

The problems of war work are almost over, and soon there will be no restrictions upon imports and exports requiring complicated licenses and certificates and red tape, but serious difficulties remain. As a matter of fact, the really constructive work of the Tanners' Council is only beginning. Mr. Wallin designed the wonderful machine which enabled our industry to co-operate with the Government during the prosecution of the war. It is now intended that this organization shall grapple with the complex questions of reconstruction, the safe guarding of the trade in the troublous times which are ahead.

The compulsory price-fixing of the War Industries Board developed the amazing fact that the tanning trade as a whole did not know its cost

of production. In sole leather, to say nothing of the more complicated tannages and finishes, the disparity of cost figures between different firms was so great as to amount to an absurdity. That is why a costing expert was engaged and the Council will endeavor to establish a uniform system of cost accounting throughout the industry. This is an imperative necessity if our tanners are to compete with foreign corporations and cartels in buying hides and skins and tanning materials, and selling leather in the markets of the world.

The statistical department is also of primary importance. Our trade has been handicapped for years because we did not know, but were compelled to guess, or by a process of inductive reasoning reach conclusions, as to the world's stocks of raw material for tanning. The expense involved in gathering and compiling the necessary statistics is such that it must be done by the industry collectively.

The Foreign Trade Bureau will loom largely in the future work of the Council. We cannot if we would, and would not if we could, escape from the manifest destiny of the trade which is to dominate the leather industry of the world. Without imports of hides, skins and tanning materials our industry would be practically ruined, and without exports of leather it would be impossible for our tanneries to operate the year round to anywhere near capacity. We must think in terms of internationalism whether we want to or not.

The Industrial Bureau of the Council will be compelled to face the serious conditions of industrial and social unrest from which no industry or country can escape. It is worse than folly to consider Bolshevism merely in connection with Russia thousands of miles away when as a matter of cold fact the red peril is lurking around the corner. Does any tanner think he is strong enough to meet this issue alone and with the antiquated weapons of the past?

It would be nothing short of suicidal for the tanners to resolve their organization into its component parts, or even to circumscribe its operation and activities. One of the consequential benefits of the war is the more perfect association and co-operation of firms and corporations that formerly worked at cross purposes with each other.

The Tanning School. Report by GEORGE H. RAYMOND. "Due to the war the Pratt Institute, Brooklyn, had found it necessary to discontinue the tanning school, and have since decided it would be impossible to reinstate the course as it had formerly been conducted for the Tanners' Institute; also that the Pratt management thought the work had now attained such importance to fully justify the establishment of the tanning school on an independent basis.

"The tanning school, which was organized by the National Association of Tanners, is understood to have been the only school of its kind in the United States, and the present suspension of the facility is therefore of unusual importance.

"It is believed that it is generally granted that there is a country-wide need and demand for systematic and scientific training in the art of tanning and the finishing of leather, and there seems to be considerable sentiment among many of the leading tanners of the country that from now on more attention should be given to educational work as applied to the industry, and that unless suitable facilities are made available our young men will still be required to go abroad for such training.

"During recent weeks the Council has received inquiries from about fifty young men who wish information concerning the tanning school. A great many of these inquiries are from men who are being released from war service. During the existence of the tanning school in the Pratt Institute nearly 150 students have graduated from this department, a large number of whom are occupying responsible positions in tanneries as chemists, foremen and superintendents.

"The tanning school has undoubtedly demonstrated that there is a demand in this country for educational work along this line.

"As the Tanners' Institute Fund has gradually developed a surplus, it is felt that this would form a nucleus of a larger fund which might be required to conduct the educational and research work along broader lines. A number of tanners have already volunteered to subscribe liberally to such a fund if a proper plan of future development is adopted. The Council has received several offers along this line of $5,000 and upwards, besides encouragement relating to bequests after death.

"The tanning school of the future might have a close affiliation with the research laboratory. The directors and officials of the Pratt Institute have expressed a willingness to assist us in an advisory way if it is decided to establish a tanning school under our auspices independent of affiliation with an educational institution.

"At the present time the Pratt Institute have available certain instructions in industrial and chemical engineering which it is understood they will continue and which provide a training in tanning and leather chemistry, but not as comprehensive as the former tanners' institute course. In the consideration of our future plans it has been suggested that provision should be made to include courses in tannery accounting, business administration and foreign trade."

At a meeting of the Board of Directors on February 20, the following resolution was unanimously adopted:

"Resolved, That the question of establishing a Tanning School, to be controlled by the Tanners' Council should be submitted to the members in a referendum."

This referendum was prepared and mailed to all members of the Council on March 15th, and embraced such questions as was thought would provide a full and complete expression from not only those who had previously participated in establishing the tanning school, but from other members.

Nearly one hundred replies have been received to date and are of interest, and as follows:

1. Do you favor the continuance of the tanning school? Answers: 79 yes, 10 no, 5 non-committal.

2. Do you recommend affiliating the school with one of the leading universities or technical institutions of the country? Answers: 52 yes, 17 no, 24 non-committal.

3. What educational institutions do you deem the most desirable to consider if the affiliated plan is adopted? Answers: Mass. Institute of Technology, Cambridge, Mass. (preferable); Pratt Institute, Brooklyn; Cornell University; Columbia University; Institution of Technology, Harvard; University similar to Northwestern University, Chicago; Case School, Cleveland; Hamilton, Philadelphia; Armour Institute, Chicago; University of Michigan; University of Wisconsin; University of Pennsylvania; University of Chicago.

4. Do you favor establishing the tanning school on a separate and independent basis if possible? Answers: 32 yes, 29 no, 32 non-committal.

5. What locality do you consider best for the location of the school on an independent basis? No report.

6. Would you favor in the creation of suitable funds to carry on the tanning school, a provision wherein a benefactor might at death or sooner endow the school? Answers: 70 yes, 3 no, 21 non-committal.

7. Would you be willing to contribute to the support of the tanning school on an equitable basis which a majority of the members of the Council might favor? (It is understood that your answer to this question is not binding and is for general information only.) Answer: 71 yes, 10 no, 13 non-committal.

8. Do you recommend that the Council formulate a plan to continue the tanning school and provide for its future along such lines as may be most desirable, the plan to be submitted to the members of the Council for their consideration and action? Answers: 77 yes, 5 no, 12 non-committal.

Tanners' Research Laboratory. Report by J. B. CHURCHILL. About three months were spent in outfitting the laboratory with the necessary working tables and in the installation of gas, water and electricity and its equipment with such apparatus as was absolutely necessary for the work to be undertaken. Actual work was commenced in this laboratory about April 1st, of last year; and I am pleased to present to you to-day the results of approximately a year's efforts. The force as at present organized, consists of myself as director, one assistant, a stenographer and laboratory boy.

During this period every attempt has been made to keep the cost of equipment and maintenance as low as was possible and at the same time, consistent with the accomplishment of accurate work. Perhaps no more trying period for the establishment of a laboratory could have been found than that which has just passed. This has been evidenced especially in the scarcity and high prices of both chemicals and supplies and on this

account it has been my general policy to purchase only such supplies and apparatus as have been absolutely essential for the work in hand.

I may say a word here in regard to our library. It is my desire to make the library of this laboratory as complete as possible in so far as obtaining the more important books and journals relating to the leather industry. Most of these books have been impossible to purchase during the war, some becoming available at the present time. These are being purchased as the chance offers.

I wish at this time to express my appreciation to the American Leather Chemists Association for their generosity in presenting the laboratory with the complete set of the bound volumes of their JOURNAL.

It is my desire to gradually add to our equipment such apparatus as is necessary to take care of new work as it develops and to eventually make the equipment of this laboratory as complete and up to date as possible.

A plan for the enlargement of our working force, is under consideration by myself and members of the New York Committee.

Regarding the work that has been accomplished during the past year, I would say that this may be well divided for the purpose of the present discussion into several heads.

First, co-operative work that has been carried on by this laboratory and the Bureau of Standards at Washington.

Second, the work done by this laboratory in co-operation with various committees of the American Leather Chemists Association.

Third, work which has been undertaken at the request of the Tanners' Council.

Fourth, work in which this laboratory has been independently engaged.

In March, 1918, I received a request from the directors of the National Association of Tanners, asking me to co-operate as far as possible with the Bureau of Standards in carrying out an extended test on the wearing qualities of various brands of commercial sole leather.

The principal object of this test has been to study the effect of the addition of salts and glucose to commercial sole leather and is being conducted on approximately 60 oak tanned sole leather bends, representing four commercial brands and 30 hemlock bends consisting of leather made from dried hides, 'fifteen of which contain no load and a very low water soluble content, and fifteen of which are heavily loaded. A detailed description of these tests was presented by Mr. P. L. Wormley at the joint meeting of the tanners and leather chemists at Atlantic City last May. The general plan for these tests was prepared last November by Mr. Wormley during my stay at the Bureau of Standards; both Mr. V. A. Wallin, then President of the Tanners' Council and myself making suggestions as seemed advisable.

During the past year I have been intimately in touch with the Bureau and have tendered such assistance as was possible in carrying out this

test. I have taken part in the marking and cutting of these bends into soles and preparing the samples for analysis. As these tests take into consideration the relation between the wear and the composition of the leather in various portions of the hides and the effect of the wear upon composition of the leather, it seemed necessary that a complete chemical analysis should be made of all samples before wearing and also of the worn soles. It has been in this respect that our laboratory has perhaps been able to be of the greatest assistance. Complete duplicate analyses have been made of approximately 140 samples representing the original sole leather and these have for the most part, been repeated on corresponding samples made from the worn soles.

It may not be out of place to say that nearly 3,000 separate determinations have been carried out in connection with this work. This work at the present time is nearly completed and the results will be published in the very near future in a joint paper issued by the Bureau of Standards and the American Leather Research Laboratory.

This laboratory and the Bureau have at present under way a second large test which we hope will at least form the foundation for future work, the object of which is the study of the effect of the use of different kinds of oil and grease in the dressing of leather. In this work, the Bureau of Standards is carrying out the physical tests, while this laboratory will undertake the chemical work necessary.

The leather for this work was very generously prepared and donated by one of the New York firms. It consists of three double backs of leather, each side of which has been finished in a different way. All three were tanned in the same manner up to the point of finishing. They were then split.

Back No. 1. One side was finished with cod oil and tallow by the usual method employed at that tannery. The other side of the back was finished in the same way with the exception that a mineral oil of as near the same physical properties was substituted for the cod oil.

Back No. 2. One side was finished as ordinary russet harness leather and one as black harness leather containing a much larger proportion of grease.

Back No. 3. This was split after the normal tannage had been completed and one side much more heavily tanned. Both sides were then finished in the same way as russet harness leather. It was the object of this test to study (in a preliminary way) the effect of the substitution of a mineral oil for marine oil, the effects of the use of different amounts of grease and the effects of different degrees of tannage; on the tensile strength and other physical properties of the leather.

As soon as these tests are completed, the results will be published and it is hoped that a much more elaborate series of experiments can be conducted along this line.

I cannot too strongly emphasize my appreciation of the relations existing between our laboratory and the Bureau of Standards. I hope

as time goes on that we may undertake more and more work of a co-operative nature.

It has been a long standing practice of the American Leather Chemists Association to submit to committees of their members, problems connected with the various analytical methods employed. It seems to your director, that it is only proper that our laboratory should take as active a part as is consistent with the equipment at hand. During the past year our laboratory has co-operated in the committee work.

Regarding in a general way the investigation of analytical methods by this laboratory, may I point out that while the development of an accurate analytical method is not the aim, this work is so closely connected with any investigational problem relating to research work on leather, that they cannot be separated and must go hand in hand, for without accurate methods of determination, no successful investigation can be carried out.

In this connection it may not be out of place to say that we have found in this laboratory much difficulty in obtaining accurate results in the determination of glucose by the official method; this has been confirmed by Mr. W. K. Alsop of the Elk Tanning Company. As time permits, a continued study of this problem is being made by both laboratories and it is hoped that some definite conclusion will be arrived at in the near future and the results published in a joint paper on this subject.

In addition to the actual laboratory work accomplished, this laboratory has from time to time, reported on various matters to the Tanners' Council. Perhaps the more important of these reports was concerned with the possible recovery of chrome waste and the manufacture of potassium and sodium bichromates.

In this connection may I point out the fact that as our American Chemical Industry develops, there will probably become available for the tanners, large amounts of waste chrome products which may be obtained at a cheaper figure than sodium bichromate. I fully realize that the utilization of these waste products depend in a great measure on their amount, their location and the cost of transportation. Experiments carried on by this laboratory have shown conclusively that these products can with proper care be satisfactorily used for the tanning of chrome leather by the one bath process. While no systematic survey of the amount of this material available at the present time has been made, it would seem to me that this may become an important factor in future years.

At a later date, a report was made to the Tanners' Council, on the availability of nitre cake. This report was sent out to the various members of the Tanners' Council under date of March 5th.

The above will outline briefly the more important work in which we have been engaged. It is the desire of the committee that as soon as the Government work; which is now almost completed, is brought to a conclusion, that we shall take up a systematic study of the beam house processes. This will include a most detailed study of the soaking and

liming of hides and the attempt made to determine under what conditions and to what extent hide substance is lost, etc. It is hoped and it is expected that the greater part of our time will be devoted to this work during the coming year.

The U. S. Bureau of Standards. Address by DR. S. W. STRATTON. We want the Tanners' Council, the representatives of the tanning industry, to help make of the Bureau of Standards an institution, not alone devoted to the establishment of standards, but to the elevation of standards, to the solving of problems which you need in developing your industry, and our success will depend almost entirely upon the extent to which you support it in that way. Unfortunately, the people throughout the country, especially manufacturers, are apt to look upon the Government service as something to do with regulation, and it is too often the case that a Government function is solely devoted to regulation of some sort. Now, I have often said, in fact I am proud of the fact, that the Bureau of Standards has not a single regulatory or police duty, not a single one; our work is solely advisory. In all of this work with the Government in preparing specifications and in settling disputes we feel that the Bureau should act as your representative quite as much as the Governments and it is no unusual thing for the Bureau to take up the case of the manufacturers against the Government. Our work is judicial to a large extent, we want to do what we can to see that the manufacturer and the Government buyer understand each other, that their contracts are drawn in a proper way and based upon correct standards.

The real thing we are trying to do and in which we want your assistance is to help us make of the Bureau a Research Institution of the highest order.

I will announce briefly the problems in progress or contemplated with respect to your particular industry, but please consider this as but a beginning. The problems in progress are:

(1) Co-operation with the ordinance department of the army in the investigation of equipment leather. Approximately 1,000 samples have been tested or analyzed in connection with the work of standardizing specifications. Specially prepared hides are being used in studying the physical and chemical properties.

This suggests another thing. It has been exceedingly difficult to get some of the Government bureaus to enter into work of this kind before the war, especially the military departments. Some of the bureaus of the army and navy have excellent specifications in regard to some things; in other things they are almost neglected, and now the war has taught them a lesson. The first time they bought on that scale and through it they have endeavored to get correct standards and correct specifications just as far as they could under those conditions, but these are things which should be worked up in times of peace.

If the military bureaus had standardized to a greater extent in time of peace and had given more attention to these things, that whole problem of providing supplies would have been much easier.

(2) A study is being made of the relative wearing quality of different sole leathers and fiber composition soles. This work includes service tests on soldiers at Camp Meade, policemen, and letter carriers, together with laboratory tests and analyses.

(3) A study of the effects of glucose on the wearing quality of sole leather. The results of this investigation will be published within the near future as a joint technologic paper of the Bureau of Standards, prepared by the Bureau and the American Leather Research Laboratory.

Now, in a case of that kind where there is some difference of opinion, you understand we are only trying to get at the facts. Your own representatives can keep in close touch with that problem. We assume that you want the truth, as we want the truth. We are only trying to find the facts: we aren't prejudiced in one way or another, nor do we undertake these problems in a biased manner. We simply try to get the facts with a view to determining whether or not these things should be taken into account in specifications.

(4) A study of the effects of different degrees of tannage and different methods of finishing on the wearing quality of sole leather. In work of this sort, the general plan is to make comparative tests on the two sides of a hide which have been tanned and finished in such a way as to eliminate all but one variable.

(5) A study of the physical properties of harness leather as affected by certain of the usual manufacturing processes. Comparisons are being made between:

1. Black and russet leather.
2. Lightly and heavily tanned leather.
3. The effect of stuffing with animal and mineral oils.

(1) A more comprehensive investigation of the different kinds of sole and upper leather, including physical, chemical, and microscopic investigations.

(2) In order to determine the relation between chemical and physical characteristics the following have to be taken into account:

1. Effect of the kind and degree of tannage.
2. Effect of rolling.
3. Effect of different kinds and amounts of grease.
4. Effect of water solubles.
5. Effect of acid, particularly during storage.
6. Water penetration and absorption of different kinds of leather.
7. Waterproofing compounds.
8. Leather for packings to be used at high temperatures.
9. Accelerating aging tests.

(3) Experimental tannery.

(4) Complete shoe repairing equipment (to be provided by the War Department).

(5) Space has been provided in the new industrial research building for a complete belt testing laboratory where it is planned to install a set of electric dynanometers of 150 horsepower capacity, for the investigation

of the power transmission of belting. Other equipment will be added and it is planned to review a large number of existing specifications, secure quantities of belting from manufacturers, and conduct a comprehensive series of tests in an effort to establish a standard specification for leather belting for power transmission purposes.

It has been suggested by your own members that the Bureau install a small unit, sufficient to bring to the laboratory the different kinds, that is, to vary the process so that we may have different sorts of samples. If this is done, it will be with your co-operation; your own people will take charge of it to a more or less extent, and your Research Committee will have access to the program and have an opportunity to approve or disapprove every step in it. It would be just as absurd for the scientific man to proceed along these lines alone as it would be for the practical tanner to undertake to make physical and chemical examinations alone, and my object in coming to-day is to ask you to co-operate with us in this work.

Colloidal Tannin Compounds and Their Applications. C. F. CROSS, C. V. GREENWOOD and M. C. LAMB, *J. Soc. Dyers and Col.* 35, 62 (1919). In the leather and allied industries there are two groups of factors particularly involved: (1) The time factor. It requires weeks to carry through the bleaching of fine linen goods, it takes months to produce a pit-tanned sole leather of standard quality, and years to season a timber for special structural applications. (2) The life history factor. The natural structural colloids have their individual characteristics, but a uniformity which masks extreme underlying variability; or in another aspect, a highly resistant aggregate quality, associated with extreme reactivity of component groups. The two factors are associated in their effects for the reason that the skin substance is highly reactive and changing throughout the entire process of conversion to leather. It may be, therefore, that in attempting a quick tannage, by applying a certain principle to control the main reaction between collagen and tannins, we may disturb the system in respect to secondary reactions, the results of which are factors of leather of quality. Any question of this order is decided by a test of quality, of which the standard is of empirical recognition and definition. There cannot, in the nature of things colloidal, be an "ideal" leather, for that would admit of comprehensive exact definition.

It is well known that the collagen-tannic acid reaction is of the rapid or violent order. A dehaired and purified skin, plunged into a strong solution of tannic acid, would react by strata, the reaction product of the external stratum opposing the penetration of the tannic acid, and the result would be a "case-hardened" leather.

This reaction is controlled in practice by graduated treatments with solutions of increasing concentration.

Another instance from technical practice of strong reaction-affinity, requiring control is that of the dyeing of silk, especially with modern synthetic products. In this case a certain control and regulation would

result from treatment with highly dilute solutions as dye baths, but not sufficiently for meeting all the exigencies of skein dyeing in mass. This, however, is controlled by the use of a mixture of emulsion colloids, the silk degumming liquors neutralized with acid, giving an emulsion mixture of silk-gum solids and fatty acids with neutral salts in solution. These liquors, suitably diluted as a dye reaction bath, convert the dye compounds into emulsion compounds.

In the course of investigations on the hemi-celluloses of seed endosperms, the basis of the well known tragasol preparations, the authors had occasion to study their compounds with tannic acids, which may be produced under carefully regulated conditions as homogenous reversible gels, closely resembling in "colloidal habit" a gelatin gel of 3-5 per cent. gelatin. With practical experience of silk dyeing methods, the authors were impressed with a probable solution of the technical problem of quick tannage, the hemi-cellulose-tannin compounds functioning as the intermediate controlling form of the specific reactive agent.

Experiments on a small practical scale confirmed by results, the inferences made above. A tanning liquor made up with equal parts, by weight, of quebracho extract (25-29 per cent. tannin) and tragasol gum, each previously diluted and mixed with all the precautions necessary to maintain the colloidal hydration at a maximum, was employed upon prepared pelts, with the result of producing a leather entirely free from the defects of case hardening.

Given the general idea of a vegetable tanning agent rendered sufficiently colloidal by admixture with the tragasol hemi-cellulose, to insure the tannage being restrained to such a degree as to exclude case hardening, the tanner has the choice of several methods of application. Up to the present the practical application has been confined to the tanning of sole and dressing leather. The methods of application recommended by the authors are as follows: (*a*) Placing the previously delimed and washed goods in a pit or vat, immersed, either laid flat or suspended in the tragasol-tanning extract mixture, handling the goods occasionally, and strengthening by addition of extract to replace the amount absorbed by the goods. The goods "strike through" with great rapidity, and complete permeation can, if desired, be obtained in 2-3 days, even in the case of the thickest hides. It is generally found advantageous to leave the goods in a longer time to insure a more complete combination with the nitrogenous colloid of the hide. The goods may then be put into "layaways" with liquors of 100-150° Barkometer or, after being rinsed and drained, they may be placed in warm extract. (*b*) The tannage may be conducted in the drum or Wilson tanning machine, taking the goods from about half way up the suspender round, and feeding into the drum a liquor of about 75° Barkometer, to which about 30 per cent. tragasol (calculated on weight of goods) has been adding. Drum intermittently for about 36 hours, when the goods will be completely permeated. Then the goods may be "laid away" or "extracted." (*c*) A method which is being practiced successfully is to drum the delimed goods in the strong

tragasol jelly, using 30-40 per cent. of the mixture on the weight of the delimed hide, drumming for 2-3 hours until the goods have become thoroughly penetrated and then either transfer to a pit containing strong extract or make the addition to the goods in the drum. The inter-action between the tragasol and the tannin takes place in the hides.

Which ever method is adopted it will be found that the finished goods possess a fine, smooth-textured grain and there is an absence of the graining usually noticeable on goods which have been drummed. Furthermore the filling of the interstices of the hide with the colloidal gel produces a leather having a greater plumpness in the flanks and thin portions than is generally associated with leather tanned in aqueous semi-colloidal tanning solution usually employed.

The authors state that the weight of leather produced varies, as in ordinary tanning, with the method used and the tanning materials employed. An analysis of the leather as compared with a good tannage of the West of England Standard is given as follows:

	Tragasol-tannin leather Per cent.	West of England standard Per cent.
Hide substance	34.94	39.60
Tannin and organic matter	46.68	45.50

The only tanning process in practical use, where the tanning agent is used at the beginning of the process at such a strength that no further addition is necessary to complete the tanning of the goods under treatment, it the process employed in tanning of glove leathers, using alum, salt, flour and egg yolk mixture. The restraining influence, in this case, which prevents the production of a "drawn grain" leather, is due to the colloidal mixture formed by the flour and egg yolk.

Experiments were also conducted on chrome tanning, using a colloidal gel of tragasol and basic chromium sulphate, with good results. Tannage in the colloidal gel was observed to be complete in 24 hours, and the finished leather was of greater thickness than the control run under the same conditions with an aqueous solution.

The physical chemical properties of tragasol are discussed in some detail.

G. W. S.

The Use of Sulphite Cellulose Extract in Sole Leather Tanneries. Walter Petrie, *H. & L.*, March 1, 1919. In this country, when highly oxidizable tanning extracts were first introduced, sole leather tanners experience trouble through oxidation in the dry-lofts and because of this color trouble the alkali-acid bleach method was adopted by practically every sole leather tanner.

It is customary for American sole leather tanners to "fill" their leather by the process generally known as "extracting;" that is to say, to wash the leather from the last layer, wring and then drum for an hour or so with a few pounds per side of full-strength, hot, liquid extract.

Many tanners who "extracted" found it necessary to "bleed" the leather in water, or weak liquor, for a day or more preparatory to bleaching. The use of sulphited extracts, which are more soluble and less oxidizable than ordinary, untreated extracts, have gradually grown in favor until now most tanners who "extract" are able to use "tempering liquors." These liquors are of such strength that they will neither increase nor decrease in specific gravity, the strength being regulated by the quality of extract in the extract drum. If no better material than sulphited extracts were procurable, tanners could not hope to finish their leather with less "bleeding" than this treatment calls for. By a better material than sulphited extract is meant a material that is more suitable for the purpose of a finishing extract, or in other words, an extract which, other qualities being satisfactory, is less oxidizable. Tanners in England have made more use of and have used for a longer time highly sulphited extracts, termed "bleaching extracts." They have been able to finish their leather in quite strong liquors without the bleeding which has generally been found necessary in this country.

The author claims that sulphite cellulose extracts when properly treated are less oxidizable than highly sulphited extracts and that they are largely used in "extracting" and tempering with good results because of this.

Many tanners use sulphite cellulose in the oil wheel. The leather after bleaching, is wrung and put into a wheel. While the wheel is in motion, the oils and any other materials to be added are introduced through the gudgeon of the wheel. It is here that sulphite cellulose extract may be added. It may also be used to advantage in "dry dipping" and if acidified with a little sulphuric acid it has considerable bleaching power.

G. W. S.

PATENTS.

Soluble Oil Products for Use on Leather or Textile Materials. U. S. Patent 1,289,097. R. Boehringer, Dec. 31. Soluble products adapted for use as a substitute for Turkey red oil and other soluble oils in treating leather or textile materials, are produced by treatment of mixtures of resins and animal or vegetable oils with H_2SO_4. In one method of carrying out the procedure, 25 pounds ground rosin is slowly added to 25 pounds corn oil fatty acids previously heated to about 90° and the mixture is stirred until the rosin has completely dissolved. The solution is then cooled and 50 pounds of corn oil is added followed by the gradual addition with constant stirring, of 25 pounds H_2SO_4 (66° Bé.). Care is taken that the temperature does not rise above 35° and the mixture is allowed to stand for 24 hours or until a test shows that it is soluble in H_2O (in the form of its alkali metal salts). The same treatment may also be applied to castor oil, cottonseed oil, bean oil, lard oil, cod oil, fish oils, tallow or other animal or vegetable oils or fats, and to copal,

dammar, amber and other resins. The sulphonation of a mixture of oil and resin produces a more limpid product than sulphonation of an oil alone.

Tanning Process. U. S. Patent 1,297,255. SIGMOND SAXE, New York, Mar. 4, 1918. The process of making relatively heavy leather, such as sole leather and the like, which comprises partially tanning hide in relatively weak vegetable tan liquor until it is struck through, and then filling the partially tanned hide by treatment in the drum with a stronger liquor comprising osage orange wood extract.

Tanning. British Patent 121,325. R. B. COCK and W. W. WILLIAMS, Dec. 7, 1917. Hides are tanned in a solution containing $Na_2S_2O_3$, $Al_2(SO_4)_3$, vaseline or equivalent mineral product, glycerol or lanoline, tanning extracts of myrobalans, gambier, quebracho, and mimosa, and turpentine. The process may be carried out either in a rotating drum or in pits provided with agitating means. When the drum is used, the hides are first treated with the tanning extract mixed with turpentine, and then the other four ingredients are added. In employing the pits, the treatment is started with the tanning extract and then a mixture of the other five ingredients is added at suitable intervals, the hides being transferred from pit to pit, which successively contain stronger solutions. The hides, in each case, are afterwards immersed in a mixture of tanning extract and a tanning liquor, and then rinsed, piled, oiled with a sulphonated oil, and shedded.

Tanning. British Patent 122,084. D. McCOY, Calcutta. Hides or skins are immersed in a solution of perchloride of mercury and then in a solution of formalin. Instead of two baths, the formalin may be added to the mercury solution. Other tanning agents may be employed, and a small quantity of an organic acid, such as acetic, may be added to the mercury bath.

Tanning With the Aid of Sulphonated Oils. German Patent 308,386, 16.2.16. O. ROHM, Darmstadt. Sulphonated oils from which the whole or a greater part of the soaps have been removed are dissolved in a volatile solvent, treated successively with flour and a solution of alum and salt, and then applied directly to hides.

Alkali Dichromates. British Patent 122,172. SOC. INDUSTRIELLE DE PRODUITS CHIMIQUES, Paris. Alkali chromate solution is treated with carbonic acid and ammonia, preferably in the presence of ammonium carbonate in excess. Sodium bicarbonate is precipitated and removed and the solution is then heated to remove ammonia and ammonium carbonate and lime is added to produce calcium chromate, after which the liberated ammonia is removed by distillation. Nitre cake is then added to produce alkali dichromate and calcium sulphate, the latter being removed by filtration.

Journal of the

American Leather Chemists Association

Vol. XIV | JULY, 1919 | No. 7

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Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $6.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized July 16, 1918.

AN INTER-ALLIED CONFERENCE OF CHEMISTRY.

The Editor has received from M. Jean Gerard, General Secretary of the Society of Industrial Chemistry, a brief account of the inter-allied conference of chemistry held at Paris on the 14th, 15th and 16th of April. France, England, Belgium, Italy and the United States were represented.

In private sessions the delegates determined the By-Laws of the inter-allied confederation and a council was formed consisting of two delegates from each of the represented nations.

The International Association of Chemistry, which existed before the war, has been declared dissolved and the Inter-allied Confederation of Chemistry has been substituted in its place. The Council is to assemble next at London on the 15th and 16th of July.

NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES.

The Fifth Annual National Exposition of Chemical Industries will be held in Chicago, at the Coloseum and First Regiment Armory during the week of September 22, and as usual there will be a number of society meetings held jointly with it.

THE SIXTEENTH ANNUAL MEETING.

The Sixteenth Annual Meeting of the Association was held at the Marlborough-Blenheim, Atlantic City, N. J., on May 22, 23 and 24. The meeting opened Thursday morning with an address by the President, R. W. Griffith.

The report of H. C. Reed, Secretary-Treasurer was as follows:

SECRETARY'S REPORT, 1918-1919.

Total number of Active members May 1, 1919	166
Total number of Associate members May 1, 1919	223
Total number of Mutual members May 1, 1919	32
Grand Total	421

There are one hundred and two (102) Active or Associate members of The American Leather Chemists Association, who have become "Mutual Members" of the Society of Leather Trades' Chemists.

TREASURER'S REPORT, 1918-1919.

GENERAL ACCOUNT.

Receipts.		
Cash on hand May 1, 1918		$1,711.11
Dues	$2,159.78	
Interest	20.67	2,180.45
		$3,891.56

Disbursements

Annual meeting expenses	$187.20	
Council meeting expenses	100.78	
Secretary's expenses	229.17	
Printing, postage, expressage, supplies and insurance policy	113.16	
Rebates on dues	5.00	
Dues paid to the Society of Leather Trades' Chemists	212.50	
Contribution to Red Cross	250.00	
From Journal account	272.98	$1,370.79
Balance on hand in bank, May 1, 1919		$2,520.77

JOURNAL ACCOUNT.

Receipts.

From advertisers	$1,578.51	
From back numbers	120.26	
From bound volumes	276.13	
From subscriptions	265.22	$2,240.12

Disbursements.

Journals	$1,869.17	
Reprints	127.39	
Abstracts and Translations	83.50	
Index	88.55	
Bound Volumes	98.45	
Editor's expenses	171.44	
Paid out for back numbers of the Journal	62.20	
Rebate on subscriptions	12.40	$2,513.10
To General account (Deficit)		272.98

SUMMARY.

Cash on hand May 1, 1918		$1,711.11
Receipts, General Account	$2,180.45	
Receipts, Journal Account	2,240.12	4,420.57
		$6,131.68
Disbursements, General Account	$1,097.81	
Disbursements, Journal Account	2,513.10	3,610.91
Balance on hand, in bank, May 1, 1919		$2,520.77
Balance on hand, in bank, May 1, 1919 (Forwarded)	$2,520.77	
Liberty Bond, second issue, 4%	1,000.00	
Interest on bond to May 15, 1919	60.00	
Total	$3,580.77	

Since May 1, 1919, checks amounting to $350.83 have been received.

Due from subscribers, dues, bound volumes, back numbers and subscriptions $1,022.05

Then followed committee reports by J. B. Churchill, L. E. Stacy and J. A. Wilson respectively, chairmen of their committees. F. P. Veitch delivered an address on the Action of Various Solvents Upon Leather Stuffing Oils and Greases. The morning session ended with a paper read by R. W. Frey on the Determination of Water Solubles in Leather.

The afternoon session began with a paper by Dr. Allen Rogers on the Tanning of Shark Skins. Dr. Rogers in his very interesting address told how the shark and porpoise were caught and showed samples of leather made from their skins but failed to tell us anything of the tanning processes involved. J. A. Wilson delivered an address on the Application of Colloid Chemistry to the Leather Industry which was followed by an address by Dr. I. D. Gerard on Colloid Chemistry. These two addresses provoked much interest and discussion. C. R. Delaney then read a paper on the Real American Dyestuff Industry. The afternoon session ended with a paper which was read by F. P. Veitch on Method for Testing Materials for Increasing the Water Resistance of Sole Leather.

The Friday morning session opened with a committee report by J. M. Seltzer which was followed by an address on Waterproofing Leather, by F. P. Veitch. Dr. Stagner, of the Mellon Institute read a paper by Van A. Wallin on Tannery By-Products. Much regret was expressed that Mr. Wallin was unable to be with us. An address on the work of the Bureau of Standards on the Chemical Composition of Leather, read by L. M. Whitmore, closed the morning session.

The afternoon session opened with a paper by Dr. C. G. Bumcke, on Sulphonated Oils, which was followed by an innovation—an address by a young lady chemist. Miss Baldwin's address on the Absorption of Chromium by Hide Powder was received with much interest and appreciation.

A committee report by R. W. Frey was followed by an address by Vance P. Edwards, on Waste Pulp Mill Bark as a Source of Tannin. At the conclusion of his address Mr. Edwards had

shown motion pictures illustrating the war activities of the Forest Products Laboratory.

The Saturday morning session opened with a paper by L. M. Whitmore, on the Proposed Organization of An American Standards Association. This was followed by a paper by F. P. Veitch, on the Relative Absorption of Greases by Wet and Dry Leather. After the delivery of committee reports by T. A. Faust, G. W. Schultz, C. M. Kernahan and John H. Yocum respectively, the meeting was called into executive session. The ballot for two ordinary Members of Council was counted, J. B. Churchill and F. H. Small being elected.

The report by J. A. Wilson, chairman of the Committee on the Extraction of Grease and Oil from Leather was published in the April issue of the JOURNAL. The reports by J. M. Seltzer, chairman of the Committee on the Determination of Total, Soluble and Insoluble Ash in Leather, and by G. W. Schultz, chairman of the Committee on the Analysis of Sulphonated Oils have appeared in the May issue. The President's address to the Sixteenth Annual Meeting and the reports by L. E. Stacy, chairman of the Committee on the Preparation of Leather Samples for Analysis, and by J. B. Churchill, chairman of the Committee on the Determination of Free Sulphuric Acid in Leather have appeared in the June issue.

Tannery By-Products, by Van A. Wallin; Waste Pulp Mill Bark as a Source of Tannin, by Vance P. Edwards; Kaolin for Tannin Analysis, by R. W. Frey; Leather Work of the Bureau of Standards, by L. M. Whitmore; and the Real American Dyestuff Industry, by C. R. Delaney are appearing in this issue. The balance of the papers and the discussions will appear in subsequent issues.

TANNERY BY-PRODUCTS.*

By Van A. Wallin.

In the summer of 1893 my name went on the payroll of the Wallin Tannery, Grand Rapids, Mich. It remained there without interruption until last summer. For 35 years my pay has come from that same roll. This has justified me in the past in

*Read at the Atlantic City meeting of the A. L. C. A., May 23, 1919.

claiming the tanner's right to membership in the A. L. C. A. Now I am outside of the trade. I am in the hair business and I am not sure that I can properly address you as fellow members. I am not certain what induced the Directors of the Tanners Products Co., to offer me my present position. It has been suggested, however, that only a superficial examination of my head was required to convince the Board that I must be an expert in the disposal of hair and as the company was carrying large stocks, this proved decisive.

The by-products of a tannery that are of value are not numerous. The most important come from the two surfaces of the hide or skin; the flesh and the hair. These two have gradually assumed larger importance and have come to be material items in the operation of a tannery.

Thirty-five years ago when I was learning the trade of a sole leather tanner, the hair and flesh taken from the dry hides which were then being tanned at the Wallin tannery were all dumped into the Grand River. I remember that the City Fathers questioned this easy disposal of what was then waste material on the ground that it would contaminate the stream and kill the fish. This theory was easily disproven by pointing to the schools of suckers which could be seen gathered around the edges of the pile, feeding on the offal. In those days only the best limed hair and the flesh from green salted hides were saved. Nearly all dry hide stock and sweat stock was wasted. Almost the only market for hair was in lime plaster. Since that day we have learned that even the lowest grade stock is of important value.

Co-operative effort in the disposal of these two tannery wastes seems logical and in point of fact has proven to be especially satisfactory. The value of the hair and flesh produced at the average tannery is nothing compared with the value of the leather produced from the hides that contribute the two materials. One of my friends reports that his sales of hair for the year 1918 amounted to only 36/100 of 1 per cent. of his total sales, and sales of flesh were 88/100 of 1 per cent. But in the aggregate the business is of considerable importance, the deliveries of hair and flesh to two co-operative companies amounted last year to about $7,500,000, justifying high-grade equipment, good organization and capable personnel in the work of collecting, manufacturing

and distributing. It is estimated that over 50,000,000 pounds of hair are produced in the United States annually from cattle and calf hides alone.

There is an opportunity to further widen the field of collective effort in the handling of these two important tannery by-products. While a large proportion of the business is handled by two large companies for the benefit of the contributing stockholders, still a considerable number of tanners of the country are without this service, to the disadvantage of the leather industry.

I will now refer particularly to that co-operative company of which I am the President. I can, without embarrassment, speak with considerable enthusiasm about the history of this company because I have not been identified with it in the past in any intimate capacity. It is true I have served on the Board of Directors a good many years and for a time was one of the Vice-Presidents of the company, but have not materially contributed to its success or its place of prominence in the industry.

The company was originally organized in 1885, and reorganized in 1917 under the laws of the state of Delaware.

The purpose of the corporation, as related in the charter, includes the manufacture, purchase and sale of hair, wool, fiber, retarder, bark, etc., and merchandise of every kind and description. The operation of the company as so far planned covers only tannery by-products and tannery supplies.

The stock in the company is principally held by tanners who sell their hair to the company at initial prices fixed from time to time by the Board of Directors. There are at present one hundred and twenty-nine contributing stockholders, including the largest tanners in the country producing sole, harness, belting, side upper, kip and calf and upholstering leather. Only a small part of the goat hair of the country is handled by the company and none of the sheep.

The earnings of the company, after a payment of 8 per cent. on the capital stock, are divided pro rata with the contributing stockholders.

The authorized capital stock is $2,000,000.00; the paid in capital stock as of this date is $1,695,200.00. The company owns either all or the controlling interest in three allied companies. The

principal offices of all these companies are united in the main office in Chicago.

The plants of the companies are located as follows: Chicago, Ill.; Milwaukee, Wis., two; Louisville, Ky.; Cincinnati, Ohio; Wilmington, Del.; Newark, N. J., two; South Peabody, Mass; Port Clinton, Ohio; Webster City, Iowa. Sales offices are maintained in Philadelphia and Boston.

Through the operations of the company direct or through its allied companies, products are manufactured and handled as follows:

Plastering hair, washed cattle and calf hair, washed goat hair, cushion hair, mattress hair, laundry felt, insulating felt, hard felt, such as sole felt and cartridge felt, wool blends, yarn, woolens and retarder. The total sales for the year 1918 were $7,184,354.32.

The comany has demonstrated the wisdom of co-operation. Its success has been largely due to the devotion of a comparatively few tanners, mostly Western men, who gave time to the organization in its beginning, without compensation, and who steered it through the trials of its early days under ofttimes discouraging circumstances.

The satisfactory results of the organization are attested by its growth. The sales in the past 10 years have increased over 500 per cent. The satisfaction of the stockholders is demonstrated by the fact that in a history of 32 years there have been no withdrawals of contributing stockholders from the company, except in cases where the contributor himself retired from business.

Membership in the company is open to any reputable tanner in the country. Stock is allotted in proportion to the business contributed.

Practically all of the business of the Tanners Products Co., up to the present is confined to the production and sale of hair and hair products. This unique material is well worthy of serious study from many angles. It is being investigated from the chemical and physiological as well as the commercial viewpoint. A considerable sum of money is being annually expended in work of investigation, through the Mellon Institute and also in private laboratories.

For all animal life the Creator has provided a protecting cover, a shield to the body. This protecting cover insulates the skin

from heat and cold and protects the body from bruise and abrasion. It is not supplied with nerves, is of great durability, and is not subject to decay. This protecting cover is in the form of scales on fish and reptiles, in the form of feathers on birds, and in mammals is the fine thread-like substance of many kinds and colors known as hair.

It is quite a startling fact that no species of mammals is without hair. It varies from the finest and softest down on a lady's cheek to the coarsest bristles of the hog and the stiff quills of the porcupine. The only places on the human body free of hair are the palms of the hands and the soles of the feet.

Hair is the last part of the body to decay, is believed to grow even after death, and is known to last for centuries. Even when exposed to the elements it will not deteriorate and can be dissolved only by heat under pressure or in the presence of alkalies or acids.

Hair is nature's most important covering, without which most quadrupeds would perish from exposure. Man has taken from the four-footed beasts this unique material and has used it for his own comfort and protection. The sheep, ox, horse, goat, camel and even the hog thus contribute of their coats to man's necessity.

Contrary to popular belief there is no fundamental or basic difference between the hair of a sheep, which we know as wool, and the hair from the body of the ox, or horse, or goat, or even the hog. All wool is hair. The most important difference between the hair of the sheep, which is sold as wool, and the hair of the ox is the larger diameter in proportion to its length of the latter. At what point indeed, it can be said that an animal fiber ceases to be hair and becomes wool, it is impossible to determine because in every characteristic the one class by imperceptible gradations merges into the other, so that a continuous chain can be formed from the finest and softest merino, to the rigid bristles of the wild boar.

In spite of the remarkable and valuable characteristics of hair, the material has, with the exception of the hair of sheep—or wool—a position of comparative ill repute. This, of course, is much more true of the hair taken from horse, cattle and calfskins than goat hair. A six months' study of the problem convinces me that tannery hair fails to occupy the place that it should in

industry, largely because of the attitude of the tanner himself. This, of course, does not refer to hair from the sheep and in the balance of the paper when I refer to hair I will use the word in the narrower sense referring only to the hair of horse, cattle and calf, and goat.

In the first place the tanner generally does not like a hide containing a fine quality of hair. The better the hair the poorer the hide, the more hair the less hide, and the tanner wants hide values and not hair values. Consequently the hair comes into the tannery like an unwelcome baby into a home, despised by all, desired by none. This feeling of contempt I really believe has affected the entire hair industry to its serious disadvantage. The tanner takes but little interest in the hair and gives it as little care and attention as possible. It is allowed to deteriorate in piles after being removed from the hide; in many cases it is washed in such a way as to leave it as dirty as possible, lime dust, dew claws, toe nails, scraps of flesh, old rope and lime hooks are baled with the hair and forwarded to market. The result of this is the widespread impression in the minds of buyers that cattle hair is a nasty product. The reputation of the whole suffers by the inferior qualities of the worst and as a result hair, which is second only to wool of all the fibers, is frequently classed with low grade materials such as sea grass, moss, flax straw, peat, and excelsior, and often has had to be dumped into the fertilizer trade at a value based merely upon its nitrogen content.

The extensive use of sulphide of sodium in the beam house has come to be a very serious damage to many kinds of hair. The sulphide is used in various ways but wherever it comes into intimate contact with the hair either in paste form or in strong solutions it is destructive. Here especially is revealed the tanner's contempt for the hair which he is willing to sacrifice, even entirely, if by so doing he secures or thinks he secures an improvement in the skin. Looking at the matter from the standpoint of the hair manufacturer it would be better to entirely destroy the hair and wash it into the sewer, as some tanners do, than to so handle the beam house process as to damage the strength of the fiber, placing on the market a hair that can never be fully satisfactory and yet worth too much to throw away. Where a small percentage of sulphide is mixed with the lime

liquors the hair is much improved by washing or rinsing immediately after unhairing the skin. In fact in any beam house process the best hair is obtained where the hair is promptly washed. A simple trough washer ought to be placed under every unhairing machine. This would not fully cleanse the hair but would remove the strong alkalies and prevent the damage that so often follows when hair is held hours, or even in some cases days before washing.

It is my belief that through co-operative effort the tanners have it in their power to lift the hair industry on to a higher plane of reputation which will result in a material increase in its value. Beginning at the beam house and continuing through the various stages of production I see no reason why hair cannot be made just as sweet and attractive and popular as wool. It is true that because of the character of the staple it can never bring the price of wool. It can be used for spinning only in the coarser grades of yarn or in small admixtures with wool and hence can never equal the price of high grade spinning materials. Still in a variety of ways, some already developed and others to be developed, it seems probable that high grade hair marketed in a high grade way will ultimately find a wide field of usefulness.

Much the largest item of hair is that produced from cattle. A small proportion, about 5 per cent. is white, the rest, all colors mixed, is named from the dominating shade, "brown cattle hair."

This most important production is graded principally as to variations in length into five principal selections: Short felting, medium felting, medium spinning, long spinning and special long.

In addition to these standard selections there is also the unwashed or limed hair used in the lime plaster trade, fuzz or hair too short for felting, and damaged hairs which are used by fertilizer and ammonia manufacturers and in the manufacture of retarder.

Retarder is a material used in the so-called hard wall plaster industry. Hard wall plaster is rapidly replacing the old fashion lime mortar in the building trade. It is made from gypsum which is hydrated calcium sulphate containing 20 per cent. water. Gypsum is found in beds throughout the United States and the manufacture of its products such as stucco or plaster of Paris is very extensively carried on. Stucco, as is well known, sets or

crystallizes very quickly when moistened with water and returns to its original insoluble rock formation. This process of crystallization is, in fact, too rapid for ordinary wall plaster as it does not give the operator a sufficient amount of time to properly apply the plaster to the wall and smooth and finish the coat. To delay or retard the time required in setting, a material called retarder is introduced. The exact chemical reaction of this retarder is still somewhat of a mystery but it is known that the introduction of a colloid delays this process of crystallization. Many different materials have been used for this purpose, but it is generally agreed that the most reliable retarder is manufactured from hair. The process of manufacture, in brief, consists of the hydrolization of the hair by cooking it in the presence of alkalies, drying the resultant solution and reducing it to a fine powder. About 8 pounds of retarder introduced into 1 ton of stucco delays the time of setting, which without the retarder would be about 15 minutes, to a period of from 2 to 3 hours.

The largest use of hair for manufacturing purposes is in the various felts. Hair felts vary from the thick, loosely felted goods which are used for upholstering and insulating purposes to the thin, hard felts used for shoe soles, washers and cartridge wads. Hair felt is recognized as the best insulating material available for refrigeration plants and is used on the majority of refrigerator cars in this country. Hair felt provides not only the best insulation from heat and cold, in which service indeed it but utilizes the qualities nature has given the material of which it is made, but it is used as a non-conductor of sound. For this purpose a special acoustic felt is made which is used in offices, halls and building construction generally.

Standard hair felt reinforced with a fabric is used in laundry machinery as is also a more expensive material known as punched felt.

As an upholstering material, hair felt has a wide field in the furniture and automobile trade as well as in car seats; indeed, wherever springs are covered with a firm pad nothing equals hair felt.

A higher grade felt in which the hair is more carefully carded before felting and the fabric fulled after felting also uses large quantities of hair. In this class of goods we find the shoe, sole,

cushion, polishing and cartridge felts. In the last named the very longest and highest priced brown cattle and calf hair is used, while in the insulating felts, short and medium hair is used.

Low grade goat hairs are used for stuffing in the upholstery trade and also in the ready made or hard wall plaster trade. The better grades of goat hair go into the spinning trade where they bring high prices especially as a blend with coarse wools. This is also true of the long spinning hairs of the calf and cattle. In the white, these hairs bring as high as 26 cents per pound.

Hair is now successfully blended with wool, producing yarn and cloth in many cases believed to be equal in quality to pure wool, and superior to wool and cotton, or wool and shoddy mixtures. Especially in the carpet industry there is a large use of spinning hair. Calf hair is used in the manufacture of plush.

Except in curled hair, which is an entirely separate industry in which the tanner is not interested, the bedding field is as yet closed to hair. Undoubtedly hair has important advantages over any of the fibers used in this trade. It is, next to wool, nature's most valuable insulator and cushion. It is almost indestructible, warm and resilliant. If the principal objection, a reputation of being unclean, can be overcome, it would seem possible to put hair into the mattress and comfort trade.

To overcome this evil reputation, to put the hair business on a higher level, I conceive to be, perhaps, the most important task ahead. The co-operation of the tanners is required to bring about success.

WASTE PULP MILL BARK AS A SOURCE OF TANNIN.*

By Vance P. Edwardes.

The possibility of a shortage of tanning material was brought to the attention of the Forest Products Laboratory, in the Spring of 1918, by the Tanner's Council of America through the Washington office of the Forest Service. It was found that this short-

NOTE: The companies which actively co-operated in this experiment were the Marathon Paper Mills Co., the Bayley Manufacturing Co., and the Pfister & Vogel Leather Co. The section of Leather and Paper of the Bureau of Chemistry made analyses on all bark samples. Credit is due these organizations for their timely assistance.

*Read at the Atlantic City meeting of the A. L. C. A., May 24, 1919.

age, while not very serious at that time, might become acute during the coming year. There were two principal causes for this situation: First, a lack of labor in the woods for peeling and barking; and second, the shortage of ships for the importation of foreign materials such as mangrove bark from British Guiana; quebracho from South America, Italian sumac, etc.

In the latter part of 1915, this laboratory issued a report by Messrs. Kressman and Thelen, entitled "Report of Barking, Drying and Analysis of Hemlock Bark Rossed at Escanaba, Michigan." Briefly, the work covered the removal of bark from logs by a special barker, the drying of the bark on a small scale by three different concerns in as many types of driers, and the analysis of material from each step by four different laboratories. The conclusions with regard to the barker are not of particular interest at this time; but the results of drying tests brought out the fact that there was little, if any, loss of tanning material during the drying operation either by direct heat or under a vacuum system. Estimates were made of cost of plant equipment capable of handling this material and preparing it for tanner's use, figures for which were obtained from the various manufacturers co-operating. These figures held out promise of low plant and operating cost, together with a rather high return on the investment. Although the results of these tests were indeed promising, nothing further was done with the matter.

The raw material as obtained from the pulp mill will run in the neighborhood of 50 per cent. moisture content. That is, half of the wet weight of the bark is water. The necessity for drying is two-fold. The most important reason is that the growth of mould in the bark must be prevented. There is no question but that the deterioration and fermentation of wet bark is due to the action of various moulds, yeasts and bacteria. This type of decomposition does not take place, however, in dry bark. Another reason is that when it is necessary for the material to be shipped some distance, it is as cheap to drive off the excess water as to pay freight, if not cheaper.

As a result of a visit made to the various concerns interested in this problem, arrangements were made for undertaking, on a semi-commercial scale, drying experiments to determine the value of this material as a source of tannin. Experimental drying runs

were made on paper mill bark during the latter part of June and the first week of July of the past year. In outlining these experiments, it was hoped to obtain a temperature greatly in excess of that necessary for economical drying of the bark in order that the effect of higher temperatures upon the tannin content of the bark might be studied. Unfortunately, because of boiler conditions, it was impossible to obtain a temperature of the drying air in excess of 200° F., which limited the bark temperature to about 70° below that until the bulk of the moisture had been expelled.

The bark was received in sacks and lost 13 per cent. moisture in transit. According to grab samples, the moisture content of the material dried varied from 28.4 per cent. to 36.1 per cent. The bark was obtained from green logs and removed in the revolving drum type of barker. It was then run through an ensilage cutter to reduce it to a satisfactory size for drying and sacked for shipment.

In its essentials, the drying equipment consisted of a source of steam, six large heating coils, a large blower fan, a long transmission line of galvanized iron and a second blower fan about 36 inches in diameter, located adjacent to the drying bed and directly connected to a small steam engine. The drier was made of sheet iron 10 feet square and about 30 inches high. This was divided horizontally by iron screening supported on light frames. The air from the fan was admitted in the middle of one of the sides underneath the screen and the bark was piled on the top to a depth of about 10 inches. A Pitot tube for measuring the air volume was installed in the suction line to the fan. The thermometer used for determining the temperature of the drying air was hung in the fan discharge and the four thermometers for obtaining the bark temperatures were embedded about 5 inches in the bark at the four corners of the drier. A manometer for measuring the static pressure under the bark bed was also installed. Wet and dry bulb temperatures were taken of the air issuing from the bark bed, in order to determine the drying efficiency, and, for purposes of calculation, the temperature of the incoming air at the steam coils was observed at the beginning and end of each run. Readings on all the instruments were taken every 15 minutes, but the air volumes were calculated on the average of the Pitot tube readings. Prior to the test, the constant for the Pitot tube was determined by two traverses of the

pipe at right angles to each other, and was found to be 97.4 per cent.

Because it was not economical to operate a large drier of this type in which the resistance of the material to the passage of the drying air exceeds 2 inches water gauge, it was necessary that the resistance of the experimental drier should not exceed ½ inch, inasmuch as the larger driers pass the air back and forth a number of times. With the intent of determining this limit, a few sacks of bark were loaded on the drier to a depth of about 2 inches. Steam was turned on in the coils and the fans started. It was found, however, that under these conditions, the static pressure was less than 1/10 inch. This was called run No. 1 although no record was kept of the bark condition. Run No. 2 started rather late in the day and it was necessary to let stand over night, after which it was started up again in the morning. Just what effect the break in drying may have had is not known; it would, however, affect only the drying calculations and not the tannin content.

As the usual amount of air required in this type of drier for economical operation is about 50 cubic feet per square foot of drying surface, it was determined in the following runs to blank off half the drier in order that the air volume per square foot might be increased since it was impossible to increase the total volume of air and at the same time maintain the temperature.

Some 6 weeks after the first group of four experiments had been made, test No. 5 was started, with bark which had been more finely divided. This bark had been prepared at the same time as that previously dried. The main reason for making this test was to determine what changes in drying conditions, if any, were to be expected upon drying more finely divided bark; and incidentally, the effect of storage in sacks upon the green bark could be observed.

The conditions under which the various runs were made are set forth in the tables and need but few comments. The variations noticeable in the readings of the four thermometers placed in the bark are due to the uneven distribution of the drying air. This could be remedied by the installation of proper baffles in the plenum chamber. The temperatures of the exhaust air were obtained by placing a wet and dry bulb thermometer near the

center of the bark bed and indicated the progress of the drying. On each table has been noted the tannin content of the dried bark as determined by the two laboratories. In the case of run No. 2 the two values of "cubic foot of air per square foot of drying surface" apply to the two portions of the run.

The analytical data indicate the results obtained under the various drying conditions. As was expected, the green bark dried in run No. 5 had deteriorated from a tannin content of 10.2 per cent. to one of 9.5 per cent. This difference would doubtless be more noticeable had the bark been stored in bulk. The results as received have all been calculated on a bone-dry basis in order that they might be more readily compared. The analysis of tannins is a difficult proceeding and variations of the magnitude indicated in the results of the two analyses can very well be charged to inaccuracies in sampling, doubtless due to the presence of slivers of wood. In any case, the results are confirmatory in that they show the bark has not been injured by the drying process.

EXPERIMENTAL BARK DRYING.

Run No. 2.

Wet bark	1,785 pounds
Dry bark	1,229 pounds
Loss	31.1 per cent.
Depth of bed	10 inches
Bark temp.	78° F.
Total drying time	3⅔ hours
Maximum air temp	200° F.
Maximum bark temp	185° F.
Moisture in wet bark	36.1 per cent.
Moisture in dry bark	4.9 per cent.
	31.5
Cu. ft. of air per sq. ft. of drying surface	27.9
Tannin content of bark after drying (bone dry basis)	11.35 per cent.
	10.50 per cent.

Bark temperatures 1 °F	2 °F	3 °F	4 °F	Room temp. °F	Exhaust air Temp. °F	Exhaust air Hum. Per cent.	Static press. In.	Velocity press. In.	Drying air temp. °F	Incoming air Temp. °F	Incoming air Hum. Per cent.
				90			0.22	0.47	193	92	34
93	93	93	91	91	93	97	0.225	0.475	195		
95	95	95	93	91	94	89	0.16	0.34	196		
95	95	95	93	91	93	91	0.18	0.395	195		
	95	95	93	91	93	91	0.17	0.39	195		
	100	100	97	93	94	90	0.17	0.405	196		
158	100	109	100	93	94	89	0.16	0.405	196		*
172	111	117	109	93	95	87	0.18	0.52	198		
183	126	122	122	95	99	75	0.16	0.485	200		
185	135	139	118	95	99	73	0.14	0.36	200		**
122	90	113	116	82			0.14	0.37	160	80	53
158	149	158	156	80			0.13	0.36	155		
154	149	156	162		124	**	0.13	0.34	150		***
169	158	165	167	91			0.11	0.31	170		
175	165	169	169	93			0.15	0.28	175		****

* Down 4 minutes.

** Shut down—(time of run 2 hrs. 25 min.)

*** Down for ½ hr.

**** Down.

EXPERIMENTAL BARK DRYING.

Run No. 3.

Wet bark	885 pounds
Dry bark	659 pounds
Loss	25.5 per cent.
Depth of bed	10 inches
Bark temp	79° F.
Total drying time	3½ hours
Maximum air temp	195° F.
Maximum bark temp	194° F.
Moisture in wet bark	
Moisture in dry bark	2.8 per cent.
Cu. ft. of air per sq. ft. of drying surface	47.2
Tannin content of bark after drying (bone dry basis)	9.04 per cent.
	10.02 per cent.

Bark temperatures 1 °F	2 °F	3 °F	4 °F	Room temp. °F	Exhaust air Tem. °F	Exhaust air Hum. Per cent.	Static pressure In.	Velocity pressure In.	Drying air temp. °F
79	79	79	81	57	72	73	**	**	172
90	90	90	109	60	76	55	0.44	0.35	183
95	122	130	162	61	76	55	0.27	0.21	185
122	144	132	183	62	77	63	0.25	0.21	189
104	167	158	185	63	78	60	0.26	0.23	185
100	176	158	187		90	99	0.25	0.24	184
106	176	167	189		89	98	0.25	0.24	185
124	179	176	189	80	89	98	0.25	0.24	195
164	185	178	190		89	100	0.21	0.20	195
176	181	181	190		96	79	0.24	0.24	195
181	185	185	192		90	98	0.22	0.22	190
185	185	185	194		92	84	0.23	0.23	195
183	187	189	192		102	56	0.21	0.21	195
187	187	187	192		120	**	0.22	0.22	195

EXPERIMENTAL BARK DRYING.

Run No. 4

Wet bark	894 pounds
Dry bark	701 pounds
Loss	21.6 per cent.
Depth of bed	10 inches
Bark temp	75° F.
Total drying time	2½ hours
Maximum air temp	131° F.
Maximum bark temp	131° F.
Moisture in wet bark	36.0 per cent.
Moisture in dry bark	14.7 per cent.
Cu. ft. of air per sq. ft. of drying surface	64.4
Tannin content of bark after drying (bone dry basis)	10.20 per cent.
	10.50 per cent.

Bark temperatures 1 °F	2 °F	3 °F	4 °F	Room temp. °F	Exhaust air Temp. °F	Hum. Per cent.	Static press. In.	Velocity press. In.	Drying air temp. °F	Incoming air Temp. °F	Hum. Per cent.
75	75	75	75	70			0.39	0.46	130	74	62
81	79	81	83	**	79	95	0.35	0.40	131		
83	82	28	111	74	80	99	0.375	0.465	127		
87	100	83	120	74	80	100	0.355	0.45	131		
95	104	86	122	75	80	100	0.36	0.48	131		
102	110	93	126	75	82	92	0.37	0.49	130		
111	113	93	128	77	88	70	0.33	0.46	130		
113	115	104	128	80	83	85	0.29	0.38	131		
118	116	111	130	80	82	92	0.27	0.38	130		
118	120	124	131	80	86	85	0.35	0.52	131		
122	122	124	131	82	**	**	0.29	0.42	131	79	60

EXPERIMENTAL BARK DRYING.

Run No. 5.

Wet bark	534 pounds
Dry bark	451 pounds
Loss	15.5 per cent.
Depth of bed	7½ inches
Bark temp	72° F.
Total drying time	45 minutes
Maximum air temp	195° F.
Maximum bark temp	189° F.
Moisture in dry bark	8.2 per cent.
Cu. ft. of air per sq. ft. of drying surface	54.8
Tannin content of bark before drying (bone dry basis)	9.4 per cent.
Tannin content of bark after drying (bone dry basis)	9.1 per cent.

Bark temperatures 1 °F	2 °F	3 °F	4 °F	Room temp. °F	Exhaust air Temp. °F	Hum. Per cent.	Static press. In.	Velocity press. In.	Drying air temp. °F	Incoming air Temp. °F	Hum. Per cent.
100	131	167	165	74	91	100	0.36	0.33	165		
135	162	158	176	76	112	48	0.29	0.31	185	74	78
182	180	189	189	80	***	**	0.35	0.34	195		
**	**	**	**	**	**	**	0.29	0.31	195	Down	

RESULTS OF ANALYSIS OF DRIED TAN BARK.

Run No.	Moisture	Total solids	Soluble solids	Non-tannins	Tannin	Insolubles
Green Bark	*34.60	16.93	14.99	6.65	8.34	1.94
	**15.80	18.20	16.20	5.80	10.2	1.9
1	* 6.82	21.4	17.50	6.8	10.75	4.2
2	* 7.08	21.8	18.00	6.7	11.35	3.8
	** 9.5	19.1	16.9	6.4	10.50	2.4
3	* 5.85	18.5	15.8	6.8	9.04	2.6
	**10.0	17.9	16.1	5.9	10.20	1.8
4	*14.23	18.9	16.7	6.5	10.20	2.2
	**12.10	19.6	17.1	6.6	10.50	2.5
Green Bark	15.5	19.4	16.4	7.0	9.4	3.0
	15.9	18.3	16.0	6.5	9.5	2.3
5	9.4	20.0	16.8	7.4	9.4	3.2
	7.9	16.9	14.7	5.8	8.9	2.2

In the opinion of the laboratory the best procedure for commercial operation will be to put the bark through a cutter, screen the resulting material, discard the fines and return the oversize for recutting. By so doing, far more rapid and efficient drying and leaching can be carried on. A large percentage of either fines or oversize will prevent the rapid leaching of the bark, and the presence of quantities of oversize will necessarily lengthen the time of drying. This procedure places no obstacle in the way of commercial production of waste bark, and will yield a product better adapted for both drying and leaching.

An important feature in the preparation of bark which must not be overlooked is the reduction of the wood content to a minimum. While the presence of wood is not deleterious to the material tanned, it is a dilutent and should be avoided. To get rid of it, hand sorting of the material coming from the barkers will probably be necessary, but this, it is believed, is not out of the question. Uniform quality of the product is important from the tanner's point of view, and every effort should be made to meet this requirement.

The state of Wisconsin produces nearly half of all the hemlock used for conversion into pulp, and an estimate of the amount of bark available from this source may be made from the pulp wood consumption figures for 1917. These show a total consumption of 442,666 cords of hemlock by the various paper mills in the state; of this amount, 90 per cent. was received in the rough.

The amount reported, 443,666 cords, is 55 per cent. of the total amount of wood consumed by the various paper mill operations in Wisconsin. If all the bark from this wood could be utilized

for tanning purposes, about 44,000 cords would be made available, which would represent a total money value of nearly half a million dollars at the mills.

The situation in other pulp producing states is shown in the following table:

State	Hemlock pulp wood consumed 1917	
	Cords	Per cent.
Wisconsin	443,666	57.2
California, Oregon & Washington	148,444	19.2
Michigan	50,373	6.5
New York	35,944	4.6
West Virginia	23,774	3.1

Unfortunately, it has been impossible to obtain figures later than 1909 on tan bark consumption, but the indications, at least up to the time this country entered the war, were that the use of the hemlock bark was rapidly decreasing, while that of extracts, particularly those of foreign origin, was as rapidly increasing. However, this condition was reversed by the causes previously mentioned; that is, shortage of woods, labor and of ship bottoms, and at the time this investigation was undertaken, it was greatly feared that the shortage of tanning material would soon become very serious. Estimating the tan-bark consumption for Wisconsin alone as 150,000 cords a year, it would be possible, if all the hemlock bark from paper mill operations could be utilized, to supply about 55 per cent. of the requirements. Had the conditions of the past year been maintained, it is estimated that the bark and extract supply would have been exhausted by February 1, 1919.

Another possible source of hemlock bark depends upon the development of a successful log barker. A number of concerns are now working on the proposition, one of which is well advanced towards success, but there still remain many difficulties in the way of commercial operation. If all the bark from the hemlock lumber industry could be recovered by the means of some such barking process, there would be more than enough to supply the needs of the tanning industry.

The utilization of this waste material would mean, first of all, a conservation of our forest resources. The lumberman would avoid increasing difficulties of obtaining satisfactory bark peelers

and would avoid completely the fire hazard and expense incidental to the peeling and seasoning operations. The tanner would gain by having a constant daily supply of dried bark, which would allow him to carry much less material in stock, to reduce his fire hazard and do away with the necessity for carrying depreciation and interest charges against a yard full of leaf bark. The benefits accruing to the paper mill would be the successful solution of what is sometimes a serious stream polution problem and the opening up of a source of income from material which now has little or no value.

Operations on a commercial scale were undertaken several months ago and aside from the amount of foreign matter present in the bark, the material was satisfactory from the tanners' standpoint. Very recent developments have indicated that there is a possibility of establishing a centrally located extract plant to be supplied with dry bark from various mills in the vicinity. The indications are that it will be unnecessary to sack the bark prior to shipment, as it can be handled very satisfactorily in the loose.

While it is too soon to quote any definite cost figures, all estimates point to the production of this material at a price which would not only enable the tanner to obtain bark at a lower figure, but provide a satisfactory source of revenue to the paper mill.

The work on this problem is by no means at an end and data on semi-commercial and commercial runs will soon be available.

THE CHEMIST AND THE INDUSTRY.*

By Fred A. Vogel.

It gives me great pleasure to be able to address such a representative audience of American leather chemists as is gathered here to-day.

For the past 15 months, I have been actively engaged in what might be called Governmental work and in these activities I have come in contact with a great many people, not only connected with the leather trade but interested generally in the development of our national commerce, both at home and abroad. The problems of American industry were presented to me in this respect

*Address that was to be delivered at the Atlantic City meeting of the A. L. C. A. but Mr. Vogel was unable to be present on account of illness.

in all their phases. The leather industry of this country is one of the greatest and most important of all industries. It is by far the most important leather industry in the world. Its development has been great. Men of genius, insight and initiative have built it to its present structure. Still I cannot help but feel that the future can be as fruitful of attainment as the past has been. We are, as an industry, big buyers of raw material. The very fact that we should be able to take hides and skins from the various parts of the globe to America, manufacture the same into leather and return them very frequently to their place of origin and sell them at a profit, is a very good evidence thas as technical men we are successful in industry. We all realize that we have gone through a period of great disturbances and that many of our usual activities have been superseded by emergency measures. We all know that readjustment is at hand. We all know that those who are most resourceful will be the ones who will survive. The Central Empires, though they have succumbed to the superior forces which opposed them in 4½ years of war, will soon rear their heads again in the commercial life of the world. The punishment meted out to them demands the resumption of all their commercial activities at the earliest possible moment. America, with its gold and its ability to give credit, will be one of the big nations to extend to them the first hand of understanding. Friendship cannot exist at once, but commercial assistance will be given at a price at which they will be able to resume. This is a necessity. At the same time, in meeting this necessity we are not without our dangers. The great efficiency of foreign competition will immediately make itself felt. This perhaps cannot be entirely confined to our erstwhile enemies, but will probably be felt upon the revival of trade amongst our allies. How then are we to meet these new activities of our friends and also of our former foes? We have had a very fair development of the leather business in this country, as we all know, but we must develop still further to be able to maintain the position that we have gained. The industrial man, in order to gain the advantages that he should, necessarily must depend upon bright and technical assistance and you men who are gathered here to-day are the foundation stone on which the American leather industry must build for the future. The earnestness with which you accomplish

your tasks, the thoroughness with which you tackle your problems, and the efficiency which you develop in the plants, are the real leads which will spell the word "progress" for our tanning industry. It has often been the experience of the practical man that the technical master has not always been able to co-ordinate his highly trained and scientific mind to the ordinary problems of the day.

I have been asked by your President to address you and I am going to address you very plainly and frankly on what I believe is one of the greatest and most important factors in our industry. Many men who are the heads of tanning establishments to-day cannot grasp the value of economical or technical knowledge. They do not see the value of minute application of correct principles. They cannot understand, or do not seem to understand, the criminal wastes that are occurring in the manufacture of leather to-day—not only wastes of material but wastes as to quality and results. I firmly believe, gentlemen, that there is more material ruined in our industry every day than any of you imagine, and, if figures were available it would be a most astounding revelation to all of us. Our industry now needs and demands more than ever, with international competition ahead of us, the best and deepest thought as to efficiency and progress. Our industry is sorely in need of men with interest and with vision. It needs progressive spirit in all that it means, but needing this, we must face the issue and ask, "Do we get it?" You men who are gathered here to-day can give it. You can give it by making practical those fundamentals which you have learned to observe. It is perfectly clear to me that our industry has ample men who are experienced and trained along technical and economical lines to carry it forward to that point of efficiency that will command respect, but to get that efficiency, to get that progress, you must all emancipate yourselves to a greater degree from the stayed activities of the laboratory and participate far more actively in the every day routine of making leather than you have. I do not want to say this disparagingly at all, but it is perfectly obvious to me that many technical men become so engrossed in the studious end of their vocation that they dream and forget the practice. It is one of the gravest mistakes that a bright and active mind can make. Its work will not survive as it

might if one would couple the wonderful training of science with industry rather than lay out the science as science itself. It is perfectly clear to me that we will be able to survive all competitive struggles if we can combine that knowledge which you gentlemen possess with a knowledge of the practical producer. Co-operation, gentlemen, is the word which has been used so frequently and "co-operation" it will be again in this case. There is only one thing that is needed for perfect co-operation and that is the sinking of the selfish ego on the part of the collateral. If we forget ourselves, we forget the other fellow, and in the forgetting of these principles and in the working together to the great and common success we win by mastering those problems which could not be solved in any other way. Co-operation between the technical mind and the practical organizer in our industry is a wonderful thing. Those who have solved that problem of co-operation are the successful leaders of our industry to-day.

I cannot add anything further, but in closing I only want to repeat what I have said before—that our industry to survive, to be successful, to be the leader in the world's leather trade, must have for the future the heartiest and utmost co-operation of its technical men with their practical leader. If this can be accomplished I can assure you that the range that exists on both sides will be equal to the highest development of any international competition that may be met.

KAOLIN FOR TANNIN ANALYSES.*

By R. W. Frey.

For the past two years there have been more or less vague complaints by the members of the Association concerning the quality of the kaolin for use in tannin analysis. Because of this, the suggestion was made, that it would be desirable to devise specifications for a satisfactory kaolin and to locate a deposit of such a kaolin so that it could be distributed to the members of the Association from a common source, similar to the present procedure for hide powder. While progress sufficient to perfect this rather ideal, yet doubtfully practicable arrangement, has not been made, some work has been done and this opportunity is taken to record the results and to bring up a discussion of the subject.

*Read at the Atlantic City meeting of the A. L. C. A. May 23, 1919.

To gain some idea of the purity and quality of the domestic commercial products an effort was made to secure directly from the source, samples of washed kaolins and after much delay the following six kaolins claimed to be representative of the normal output were obtained:

Text reference	Source	Treatment	Color
A	McIntyre, Ga.	Washed without chemicals.	Pale bluish white
B	Gordon, Ga.	"	"
C	" "	"	Dirty white
D	Spruce Pine, N. C.	Washed without chemicals. Alum used for settling.	Pale yellow
E	Dry Branch, Ga.	Washed without chemicals.	White
F	Congaree, S. C.	Washed.	White

Upon receipt the samples were thoroughly dried at 100° C., passed through a 20-mesh sieve and bottled. These samples will be referred to in the text "as rec'd." Portions of each sample were digested for about 24 hours with 5 per cent., by weight, of actual HCl and after washing repeatedly with distilled water until the washings were practically free from chlorides and were neutral to phenolphthalein, were dried and bottled. These samples will be referred to hereafter as the "HCl Washed Kaolins."

Soluble Matter.

The kaolins were examined for solubility: (1) in water as prescribed by the present test under kaolin; (2) in 0.02 normal acetic acid, and (3) in 0.5 per cent. clear tannic acid solution. For acetic acid solubility 15 grams of kaolin were shaken with 250 cc. of practically 0.02 normal acetic acid and after standing 1 hour and removing 50 cc. of the solution the remainder was filtered and an aliquot of 100 cc. taken for soluble matter. For the tannic acid test a clear solution of tannic acid was prepared by dissolving a weighed quantity of commercial tannic acid in a small volume of water, filtering through a hardened filter and then diluting to the proper volume to give practically a 0.5 per cent. solution. A solution with a very slight haziness was obtained. The tannic acid solubility test was then made just as directed for the soluble solids determination using each one of the kaolins and

evaporating 50 cc. aliquots for comparison with the weight of the residue from the blank on the tannic acid run in exactly the same manner only omitting kaolin.

The results are given in Table I and they show the kaolins to be remarkably free from soluble matter when it is considered that they were prepared on a commercial scale.

TABLE I.—SOLUBLE MATTER IN VARIOUS KAOLINS.

	*Water solubles Mg. per gram kaolin	*Acetic acid solubles Mg per gram kaolin	Tannic acid test Mg. residue-50 cc. aliquots
Kaolin A—As rec'd.......	0.4	0.5	228.3
HCl washed...	0.0	0.2	
Kaolin B—As rec'd.......	0.5	0.4	227.3
HCl washed...	0.4	0.0	
Kaolin C—As rec'd.......	0.3	0.4	227.9
HCl washed...	0.0	0.1	
Kaolin D—As rec'd.......	0.7	1.1	228.2
HCl washed...	0.2	0.2	
Kaolin E—As rec'd.......	1.2	1.8	226.0
HCl washed...	0.0	0.2	
Kaolin F—As rec'd.......	0.2	0.9	227.4
HCl washed...	0.0	0.1	
Blank-Solvent + 590 Paper	0.5	0.9	227.8

*Corrected for blank given at bottom of table.

The highest corrected water soluble residue is 1.2 milligrams from kaolin E and this residue includes some very fine particles which persistently passed through the filter paper.

The other residues for water soluble fall below the present limit of 1.0 milligram. Attention should also be called to the fact that HCl washing reduced the residue in all cases to practically nothing which results do not lend evidence to the statement sometimes made to the effect that soluble matter is not decreased by acid washing. The acetic acid test is apparently a little more severe but even here four of the six samples give, as received, less than 1.0 milligram residue per gram of kaolin. It is believed that for soluble matter the acetic acid test is better than the determination of water soluble matter since it would be for some conditions more severe and does more nearly parallel the slightly acidic nature of non-tannin solutions, which of course, would include all of any such soluble matter present in the kaolin.

The tannic acid test for solubility may be considered unnecessary but it is suggested as of value for another purpose. It has been frequently found that kaolins produce a decided discoloration with tannic acid solution, a fact which is of importance, at least in color measurements. The discoloration which varies from brown to greenish brown generally persists even after discarding the solution used for the hour's preliminary digestion as for soluble solids. Kaolin A gave a noticeable discoloration; kaolin B a slight one, as did also kaolin C. The corresponding HCl washed samples were no better in this respect and if anything slightly worse. These observations are interesting when it is remembered that the water soluble matter is very low and practically nil for the HCl washed kaolins. The discoloration naturally indicated iron or possibly alkalinity. Water extracts from 15 grams kaolin in 150 cc. water after standing over night did not, however, respond to the test for iron with NH_4SCN nor were they alkaline to phenolphthalein when concentrated to a very small volume. Five grams of kaolin A which gave the most pronounced discoloration with tannic acid and 5 grams of kaolin D which showed practically no discoloration were each allowed to stand over night in 150 cc. of 0.5 per cent. tannic acid solution. One hundred cubic centimeter aliquots of the filtrate from each were evaporated and ashed. A blank was also run on the tannic acid solution. Upon testing, the ash, that from the blank and from kaolin D showed a trace of iron while kaolin A gave comparatively speaking a decided test, thus indicating that for certain conditions a reaction takes place between iron present in the kaolin and the tannic acid.

Clarifying Ability.

It is very difficult to devise a standard procedure by which the clarity can be numerically measured because of the numerous variables, such as the porosity of the filter paper, the time of filtration, and the nature of the solutions and of the insolubles. Probably the only practicable means is by actual trial under what have been found by experience to be severe conditions. From the preliminary work there did not seem to be any positive relation between the behavior of the kaolins on settling and their ability to give clear filtrates. The samples varied from one extreme to the other in settling. Kaolin F settled very rapidly

and kaolin E very slowly, the other samples were intermediate. The work on testing for clarity was not as comprehensive as it should have been because at the time the tests were being made the regular work of the laboratory was such that few tannin analyses were being run and consequently the variety of materials was not very great.

As has been suggested by several of the members fineness may be an important factor in indicating the ability of a kaolin to give clear filtrates. All the samples of washed kaolin that have been tested show that practically 100 per cent. will pass a 200-mesh sieve and for measuring fineness beyond this it would be necessary to resort to elutriation methods which of course, require special apparatus, much time, and painstaking care. If time permits, however, it is intended as a matter of interest to investigate the critical point for fineness along this line.

Since it is reputed that ignited kaolins are not satisfactory for clarity it was thought that some information might be obtained from observations on ignited portions of these kaolins. The ignited kaolins when mixed with water separated into a somewhat granular, rapidly settling portion and a very fine, extremely slow settling part which produced a faint milkiness, that was noticeable even after standing over night. When tested, however, for water soluble matter all the ignited samples gave practically clear filtrates and the residues from these filtrates, including any fine particles passing through the paper, ranged from 0.3 milligram to only 1.1 milligrams per gram of ignited kaolin. With tannic acid, though, the ignited kaolins, as a general thing, gave slightly hazier filtrates than did the corresponding unignited kaolins, and on a hemlock extract, containing about 3 per cent. of extremely fine insolubles, the ignited samples gave on an average, 5.6 milligrams higher soluble solids. This would indicate that ignited kaolins have a tendency to give hazier filtrates and judging from their behavior on settling it might be well to specify that kaolin should not, on standing over night in water, give a slightly milky supernatant liquid. It might also be advisable to state that the kaolin should not be ignited and should give, when determined after drying at 100° C., a loss on ignition of from 12 per cent. to 15 per cent. For the six samples loss on ignition varied from 13.8 per cent. to 14.5 per cent. Specifying

the loss on ignition would in addition be an indirect measure of the purity of the kaolin, assuming that by kaolin, is meant the mineral kaolinite which contains practically 14.0 per cent. water of combination.

SUITABILITY FOR USE IN DETERMINING ACIDITY OF TAN LIQUORS.

McCandlish and Lederer (This JOURNAL 12, 570) have called attention to the effect of impure kaolin on the determination of acid in tan liquors and have suggested an excellent test and one which, when slightly modified to include soluble matter, it is believed should be embodied in the kaolin specifications. The following is a direct quotation of their suggested procedure: "Shake 15 grams of kaolin vigorously with 250 cc. N/50 acetic acid and allow to stand 1 hour; withdraw 50 cc. of the settled solution and titrate with N/10 sodium hydrate, using hematine as indicator. A titration of 10 cc. and the characteristic end-point indicate that the kaolin is free from alkaline matter and sufficiently free from iron to permit its use for the purpose in view.

The six samples of kaolin, in both the "as received" and the "HCl washed" condition, were examined as follows using in general the principle of the above procedure: To 15 grams of kaolin contained in a flask, 200 cc. of water and 50 cc. of practically 0.1 N acetic acid were added and after thorough shaking, the flask was allowed to stand 1 hour. Fifty cubic centimeters of the supernatant liquid was pipetted out and titrated with 0.1 N NaOH and hematine. The remaining contents of the flask were then filtered through 590 C. S. & S., 15 centimeter filter paper, 100 cc. of the clear filtrate was evaporated and weighed as is done in the ordinary tannin analyses. A blank for both the titration and soluble matter was run in exactly the same manner omitting nothing but the kaolin. The results from the titration are expressed, simply for convenience, in cubic centimeters of 0.1 N NaOH required. The residues for soluble matter, after correction for a blank from the acid and filter paper of 0.9 milligram were calculated to milligrams of soluble matter per gram of kaolin by dividing by six.

For comparison the results are assembled in Table II together with some data previously mentioned.

TABLE II.—Suitability for Determining Acidity of Tan Liquors.

	Cc. 0.1 N NaOH for 50 cc. aliquot	Mg. soluble for grams of kaolin in water	0.02 N acetic	Discoloration with 0.5 % tannic acid as for soluble solid determination
Acid Blank.............	9.53			
Kaolin A—As rec'd.....	9.51	0.4	0.5	Decided
HCl washed.	9.51	0.0	0.2	Decided
Kaolin B—As rec'd.....	9.39	0.5	0.4	Slight
HCl washed.	9.32	0.4	0.0	Slight
Kaolin C—As rec'd.....	9.51	0.3	0.4	Slight
HCl washed.	9.51	0.0	0.1	Slight
Kaolin D—As rec'd.....	6.80	0.7	1.1	Practically none
HCl washed.	6.80	0.2	0.2	Practically none
Kaolin E—As rec'd.....	9.32	1.2	1.8	Practically none
HCl washed.	9.39	0.0	0.2	Practically none
Kaolin F—As réc'd.....	9.20	0.2	0.9	Practically none
HCl washed.	9.20	0.0	0.1	Practically none

It should be mentioned that none of the end-points were sharp, this being true to some extent for even the blank solutions, but because of lack of experience with the indicator it can not be stated whether or not the bewildering sequence of colors was characteristic. Practically all of the solutions darkened as the titrations progressed but it is believed that they were not carried beyond a point which might be mistaken for the end-point, although working under known conditions may have exerted a sub-conscious influence.

The results bring out several points of interest. First it should be noted that here again HCl washing of the kaolin and consequent reduction of soluble matter to practically nil does not seem to result in an improvement. Evidently soluble matter is no indication of the quality of a kaolin for this titration. Neither does there seem to be any significant relation between the titration and the discoloration with tannic acid.

Kaolin C was the best for the titration and kaolin A was possibly next best. Kaolin D was undoubtedly the poorest and would certainly give misleading results in acidity determinations. It is interesting to note that from the correspondence this kaolin is the only one in which alum was used for settling and that from the acetic acid residues it was the only one to give a test for aluminum. It was mentioned by McCandlish and Lederer that probably salts of other metals may have an adverse influence on

the indicator. A simple test will show that traces of aluminum salts give with hematine a color almost identical with the end-point and in fact this is practically the same thing as the qualitative test for aluminum with logwood. The solubility results would indicate, as was also intimated by the above authors, that the merest traces will sometimes produce a decided interference.

SUMMARY.

Assembling the data from various contributions on kaolin for tannin analysis the following specifications are suggested as tentative and as a working basis for correction, revision, and enlarging as experience proves advisable.

Kaolin Specifications.

(1) Should be preferably pure white, soft, smooth, free from sand and other gritty matter, and should wet up readily showing no tendency to lump or "ball up;"

(2) Should give clear filtrates with tannin solutions and on standing over night with distilled water should give a clear supernatant liquid and when filtered the filtrate should not, on boiling down, be alkaline to phenolphthalein;

(3) Should give on ignition of the dried sample a loss of from 12 per cent. to 15 per cent.;

(4) Should not give a discoloration with a 0.5 per cent. tannic acid solution when tested as prescribed by the present official method for soluble solids;

(5) Should be tested as follows: Shake 15 grams of kaolin vigorously with 250 cc. of practically 0.02 N acetic acid, allow to stand 1 hour, pipette 50 cc. of the supernatant liquid and save the remainder. At the same time run in exactly the same manner a blank on the acetic acid solution omitting only the kaolin. Titrate the 50 cc. aliquots with 0.1 N NaOH and hematine. The titration from the kaolin test should give the characteristic end-point and should not differ from that on the blank by more than 0.25 cc.;

(6) Filter the remainder from the test under (5), through C. S. & S. 590, 15 centimeter filter paper or other suitable paper, returning the filtrate, if necessary, until clear. Carry the blank along likewise. Pipette 100 cc. of the filtrate, evaporate, dry, and weigh as in the usual tannin determinations. The residue,

after subtracting that from the blank and dividing by six should not exceed 1.0 milligram.

Appreciation is expressed for suggestions offered by F. P. Veitch.

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THE LEATHER WORK OF THE BUREAU OF STANDARDS.*

By L. M. Whitmore.

Until the Armistice was signed and the Government cut down on its purchases of leather, the work of the leather laboratories of the Bureau was to a considerable extent the testing of leather for Government purchase. About 1,500 samples of sole, harness, strap and side leather were tested for the different departments in charge of leather purchases. Most of the work was done for the inspection divisions of the ordnance department and the quartermaster corps. Along with this routine work there were carried on a considerable number of miscellaneous investigations, such as tests to determine the effectiveness of different waterproofings, the water-resisting qualities of different types of leather used in shoe uppers, the heat resistance of leathers for gun packings, and the relative resistance of chrome and vegetable-tanned leathers to conditions such as prevailed in the trenches.

In addition to this work, the Bureau has undertaken an extensive investigation of sole leather with the ultimate object of determining the relation of the chemical composition and manufacturing processes to wearing quality, flexibility, and water resistance. Complete analyses are made on all the leathers tested both before and after wear in order to give data showing what happens to a leather during service. All the sole leather investigations are being carried out in co-operation with the American Leather Research Laboratory and the different tanners of sole leather.

Taking into consideration the large variation in the weight and quality of hides, it was thought desirable to run these tests as far

*Read at the Atlantic City meeting of the A. L. C. A. May 23, 1919.

as possible by the one hide experimental method. This method may be briefly outlined as follows:

The leather is run through as double backs up to the point where it is ready for the experimental treatment. It is then cut into backs or bends, and the two sides of the double back are given the experimental treatments. After this they are finished in an identical manner and tested by putting soles, cut from corresponding locations in the two bends, on the same pair of shoes. Any consistent difference in wear of the soles from the different bends should then be the result of the variation introduced into the tanning process. This method eliminates variations in the hides and also any variations in the tanning process up to the point where the backs are cut. This makes it possible to determine with some degree of accuracy the effect of the variable under consideration and to get reliable data from fewer bends than would be necessary if different hides were used. The data secured by this method are specific in that they apply to but one or two factors. If different tannages were used, the results would be reliable as far as the leathers tested were concerned, but a difference in wear could not be traced to any definite cause, as the tannages would vary in so many ways. In either method of test, there should be used enough bends to overcome the incidental variations of the test.

The sole leather investigations now contemplated or under way include comparisons of the wearing qualities of many different types of leather, such as chrome, loaded and unloaded hemlock, oak containing sulphite cellulose extract, lightly and heavily tanned oak, arctic sole, drum tanned and yard tanned oak, and stuffed and unstuffed leathers of many types. The effect of wear on the chemical composition of these leathers will be studied in detail.

The preliminary sole leather investigations, which have been completed, include a comparison of the wearing qualities of four types of commercial sole leather and the effect of wear on the chemical composition of these leathers. This work has given some very interesting data, including the complete analysis of a large number of new and worn soles from five different types of leather. The analyses were made by both the Bureau and the American Leather Research Laboratory and have thrown some

light on the analytical methods now in use. A considerable part of the data from these tests is being published as a joint paper of the Bureau and the American Leather Research Laboratory. This paper is to be the first of a series which will deal with the results of investigations of the composition and wearing qualities of various types of sole leather. The program which has been outlined for the sole leather investigations is a rather extensive one, and will take considerable time for completion. The data will be published as soon as they become available, however, as many of the tests will have an individual value aside from their relation to the problem as a whole.

Similar investigations of strap and harness leather have been initiated in order to correlate, if possible, the chemical composition with the tensile strength and buckle tests, and with the rate of deterioration in service as measured by those qualities. The factors being investigated at present are the nature and amount of grease, degree of tannage and acidity, in their relation to the physical qualities, and the deterioration of the leather. Tests made with strap and harness leather show that there is a consistent increase in tensile strength with additional grease up to a certain point, after which the addition of more grease is without appreciable effect. This point is not the same for all leathers or all stuffings, but varies widely with the nature of the tannage and the stuffing material used. As far as the immediate effect is concerned, the mineral greases appear to have as beneficial an effect as the ones of animal origin.

It is generally believed that the question of acidity is very important in these types of leather, and some tests have been started which are planned to follow the effect of acidity on the tensile strength. Harness and strap leather sides have been cut into strips large enough to test for tensile strength and the alternate strips given different treatments with acid in order to increase the amount of sulphuric acid. These sides will be kept, and from time to time tests will be made to determine the amount of deterioration in the different strips. In one series of tests made at the end of 6 months, there was no appreciable difference in the tensile strength of strips containing from 0.37 per cent. to 0.95 per cent. sulphuric acid by the Procter-Searle method. Other sides have been treated with varying concentrations of acid, but

no tests have as yet been made, as it has been thought advisable to run the tests for a minimum period of one year. The time between future tests on these sides will depend upon the results obtained in the preliminary tests. If no deterioration is evident at the end of a year the next tests will probably not be run until 3 or 4 years later.

In connection with the above work on the effect of acidity on the leather, a series of experiments is being run on the rate of hydrolysis of concentrated gelatin solutions containing different amounts of sulphuric acid. The hydrolysis in each case is being followed by the Sorensen titration, which is a measure of the free amino groups present.

Our laboratory facilities do not at present admit of much experimental work on tanning processes, but the co-operation we have received from the tanners has been so effective that we have not been handicapped in our experimental work on that account. We hope to have some facilities for chrome tanning, so that we can continue some experiments that were started on the heat resistance of chrome leathers with varying degrees of chroming. The data at present available indicate that the resistance of a leather to heat increases with the degree of chroming, as the most resistant leathers tested were the most highly chromed.

THE REAL AMERICAN DYESTUFF INDUSTRY.*

By C. R. Delaney.

During the course of certain addresses made in the past few years I do not recall any occasion when I had to preface any remarks that I was about to make with an apology. For one thing when I spoke about the matter of natural dyestuffs the subject required no such preamble, and secondly when a man feels that he has done as well as his powers permit there is nothing further to be said in relation to the matter; but at this time and for this occasion it is different.

Some months ago my very good friend, Mr. Oberfell, asked whether the natural dyewood extract manufacturers desired to make any statement concerning their business at the forthcoming

*Read at the Atlantic City meeting of the A. L. C. A. May 22, 1919

convention of the A. L. C. A. which is the present one, and to this request in an unguarded moment I acceded, and was very glad to; and when he said that I could choose my own subject I decided to confine my remarks to the Real American Dyestuff Industry, and with this in mind proceeded to secure what information there was pertaining to it. This was more of a task than might be imagined for one has to go back to the date of the earliest foundations of our Republic to find the beginning of this great though little known industry. Well, the result of this investigation produced such a tremendous array of information that it was impossible to remember it all, and notes had to be jotted down about it, and this was the occasion of my undoing.

When it has been my privilege to be permitted to speak to you before, whatever ideas I had rose Minerva-like, "full-panoplied from the forehead of Almighty Jove" or if you prefer it, jumped hot off the bat. Whatever ideas there were rattling around in my head projected themselves forth with great speed, and as much precision as under the circumstances was possible for I was seldom prepared with any detailed information and trusted to a more or less treacherous memory. But now the situation is different; having to record the notes that were so kindly sent to me by other houses in our industry I felt that it would be nothing but just to render unto Caesar that which is Caesar's and quote verbatim from some of the statements sent to me, and this time instead of being more or less at fault for lack of information I find I am too blame well prepared for there is so much to be said, and the majority of it is about our competitors. Therefore, I repeat, I have to make an apology, and this comes from the fact that I propose to inflict upon you a written speech, which after all to the majority of you will be about as interesting as some of the Government bulletins that have appeared more or less recently, even those pertaining to my own industry; yet unlike these it will have one advantage and that is that it will not attack nor harm any industry even though it shares in common with some of these reports many statements that a lot of other people have made to me, and for which I do not intend to give them any credit, or at least no more than I have to.

On May 25, 1917 at a conference of editors called to Washington, D. C., possibly for the purpose of conducting the war

from the point of view of those in power at the time, Mr. W. S. Redfield, Secretary of the Department of Commerce & Labor, felt called upon to make the following extraordinary statement: "I need hardly tell you that we had no dyestuff industry in this country or one which was existing merely by the sufferance of our friends, the enemy. I have been told at my desk, gentlemen, that Germany would not permit the establishment of an American dyestuff industry in those words, and forthwith learning that fact we set about establishing one. We have it now." This statement had the effect of causing mild wonder on the part of some of the manufacturers of dyestuffs, and the writer felt called upon to write to Secretary Redfield, and state that Dr. Norton (one of the Government exponents of the most sounding of sound knowledge, and the special agent of the Department of Commerce & Labor under Secretary Redfield) should have been able to inform the Department that there was a very thriving and enormous dyestuff industry in these United States prior to the war inasmuch as we had taken particular pains to go to Washington and complain about the harm that was being done to the dyestuff industry by this same special agent's utterances, and our company had advised him fully concerning the details of our business—what we made—how long we had been making it—to whom we had supplied it. We asked Mr. Redfield when he spoke of the dyestuff industry did he mean the little and then comparatively unimportant part known as the aniline industry or was he speaking in such a slighting manner of the enormous aggregation of capital and brains representing the natural color manufacturers. The result of this was that we received a letter from Mr. Redfield stating in part that when he referred to the dyestuff industry he meant the artificial dyestuff industry, and that he had fallen into the common error of a thousand other public speakers. We did not see, however in the *Public Press* or in any other form either apology or correction for this slur against our industry, and having no wish to become embroiled in a controversy with any political autocrat we kept quiet, although it was much against the grain.

What then is the record of the The Real American Dyestuff Industry?

According to the best information that we can find, a Dr. Bancroft, in 1795 discovered that the bark from the black oak tree—

indigenous to the United States—when ground up, extracted or boiled with water was capable of yielding a yellow dye of surprisingly beautiful and fast quality. He took his discovery with him over to the Court of George IV and there received a patent giving him the right for the sole use of the ground bark which he called quercitron, a compound of *quercus,* the oak and *citron—gelb,* golden yellow, and we assume that the tanners of the country who had been grinding their black oak ground this material for Dr. Bancroft, and it was carried over to England and thence to the Continent.

One hundred and twenty-one years ago the first dyestuff industry was started and appropriately enough it commenced in a small shop in Greenwich Village, N. Y., from which so many curious and extraordinary things eminate even unto this day, and it sometimes is a cause for wonder whether the artists' colony of the village was not primarily started there because of the fact that that is the place where manufactured natural color first commenced to be produced in our Republic.

A number of years ago Mr. Joseph E. Stevens, of the then New York Tanning Extract Co., addressed you upon the subject of the manufacture of quebracho, and in the course of his address he mentioned that the predecessors of the quebracho company had started in Greenwich Village, but he may not have called to your attention that Wm. Partridge, who founded the business which afterwards merged into the great quebracho company was not a grinder of tanning materials, but an importer, cutter and grinder of dyewoods at West Tenth St., Greenwich Village in a small mill driven by one mule. Prospering, he naturally moved out of Greenwich Village and went with his enterprise to larger quarters at Graves End Bay, N. Y. Harbor, where he built a tide mill capable of producing both cut dyewoods and extracts, operating at the same time two schooners, the Hawk and the Partridge, which delivered his raw material to New York City, and Mr. Wm. Partridge was the pioneer wood extract manufacturer of the United States, and in an unbroken succession the American Dyewood Co., The New York Quebracho Extracting Co., and J. S. Young & Co., are the outcome of his early endeavors. One hundred and twenty-one years ago that mule commenced his long grind, and from that beginning alone the inter-

national plants of the Quebracho Company, the enormous plant of the American Dyewood Co., and the four factories of our own company had their beginning. Sometimes it has seemed to us as though that mule was an epitome of the extract manufacturers, patient, long suffering, strong and determined, particularly the latter.

Going back to our subject, the old tide mill of Mr. Partridge was superseded at the close of the Civil War by a new and larger plant at Greenpoint, and after that time the consolidations commenced to go into effect. The chronological order of the companies was as follows:

Wm. Partridge
Wm. Partridge & Sons
Partridge & Harway
James L. Harway & Co.
The New York Dyewood & Chemical Co.

and at this point we will leave it for a time.

The Boston Dyewood & Chemical Co., with a factory at East Boston was established somewhere in the middle of the 19th Century, although as to its original name and date of origin I have been unable to get any information, but in 1869 certain members of the Boston Dyewood & Chemical Co., were approached by Mr. John S. Young, the founder of our business, and the father of the present President, to form an extract works at the little town of Shrewsbury, Pa., wherein to grind and extract the quercitron of Dr. Bancroft, and Flavine, which was the concentrated dyestuff which gave the color to the extract, and in that year the Shrewsbury Mills Manufacturing Co. was formed to manufacture quercitron extract for the Boston Dyewood & Chemical Co. In 1873 the name was changed to J. S. Young & Co., Ltd., and in 1892 the Boston Dyewood & Chemical Co., consolidated with the New York Dyewood & Chemical Co., and formed the New York and Boston Dyewood Co.

In 1835 the firm of John M. Sharpless & Co., was established at Waterville, near Chester, Pa., and continued under the same name until 1882, then beginning a corporation known as the Sharpless Dyewood Extract Co. Two years after the incorporation of the Boston Dyewood Co., with the New York Dyewood

Co., the consolidated company known as the New York & Boston Dyewood Co., was consolidated with the Sharpless concern under the name of the American Dyewood Co., and some of the interests that were a part of the New York & Boston Dyewood Co., were sundered at about the same time. Prior to the time when Mr. Redfield spoke so illuminatingly about something of which he was in the very best of positions to know everything about, there was another American dyestuff plant which had started, according to the information that I can secure, 20 years after the formation of the Republic of the United States. This plant was put up at Stamford, Conn., and until the disastrous fire which occurred in February of this present year it had been operating continuously under practically the same name for 120 years, being held in the same family even after the incorporation which was between 30 and 40 years ago. The plant of the Stamford Mfg. Co., was the second largest plant in the world for the manufacture of dyewood extracts, that of the American Dyewood Co., being the largest individual plant for this purpose.

However, before the formation of either J. S. Young & Co., or the American Dyewood Co., John H. Heald & Co., now of Lynchburg, Va., began making flavine and quercitron liquors and extracts about 1860, on Monument St., in Baltimore. It was only a little while before their business outgrew their quarters for naturally if they were making quercitron extract we assume that everybody wanted the best yellow dyes that they could get and in 1863 they began operations on a large scale, and in addition to the materials manufactured they began to make extracts of logwood, hypernic and fustic, and in 1869, the same year that our own company was formed, they built the Lynchburg plant, and through the most courteous advices of Mr. Charles E. Heald, to whom I am indebted for this information, for the next 3 years, the principal output was flavine, quercitron and pulverized quercitron bark, and sometime later, about 1874 or '75 the firm in Baltimore sold all of their logwood equipment to what was later known as the New York & Boston Dyewood Co., so it looks as though Mr. Heald owed something to that old mule for I understand that to-day his company under the same old name is capable of turning out a barrel of completed extract every two minutes of the day, and I can well refer to Mr. Stevens' statement when

he said anyone with the money and the mill can make extract, but in these days to turn out an article of the highest quality which shall run uniform year in and year out is no child's play.

When Mr. Heald began making flavine in 1860, Mr. John D. Lewis, the predecessor of the present head of the house of the same name, commenced to manufacture logwood products in Providence, R. I., and that plant continues manufacturing to this present day.

In 1884 Mr. Francis J. Oakes founded the Oakes Mfg. Co., and in 1886 the first hematine was made by him, and was placed upon the market on a commercial basis during that year.

Prior to the war there were still a few other companies whose total output and scientific knowledge were not such as to create any very wonderful impression, but the volume of capital and magnitude of business involved in the natural dyestuff industry was immensely greater than in the artificial color business. The one exemplar of this latter had, it is true, been able to exist, in the language of the illustrious democratic secretary, "on sufferance from the Germans," but it is hardly necessary to say that with the showing made for our part of the dyestuff industry that we had existed not only in spite of the Germans, but *because* we made better dyestuffs than they did. There were dyestuff factories in Germany, France, Great Britain and Italy long before the war, but they had never been able to successfully compete against our own products because as a general rule their stuff was not as good as that made here.

I cannot speak with any authority about the other companies, but I do know before the war the Stamford Mfg. Co., shipped a very large quantity of logwood extract into Germany, and although we were not making logwood extract at that time nevertheless we shipped the major proportion of our production of flavine to Germany and Switzerland. I have spoken with a number of the manufacturers of native American dyestuffs, and while our own business prior to the war was the largest in point of view of pounds of finished material produced that it had ever been up to that time, some of the other manufacturers stated that their production had declined. This was particularly true about 1908 when the peculiar German propaganda of seeing the dyer had reached its zenith. After that time the uses of the

natural dyestuffs were brought more forcibly to the attention of the users than they had been before, and the result was a slow and healthy growth of the business. As far as we are concerned, 1913 showed us double the production of 1909, and the business was steadily increasing. Tanners, color makers, dyers and printers were commencing to swing the pendulum back and although it is impossible to collate figures showing the imports of dyewoods and the peel of quercitron bark for 20 years ago, say 1899, nevertheless I am perfectly satisfied in my own mind from the figures that have been produced from our own company that there was more natural dyestuff used in 1913 than there was in 1893. It has been stated to me that the amount of business done in the old days was greater—there were more barrels of extract. This is not true as far as raw material was concerned because in those good old days barrels and casks were pretty cheap, and the result was that 12°, 14° and 16° liquors were freely sold, both here and abroad in place of the solid, crystals and powdered product of high concentration of the present day. In 1917 when Mr. Redfield spoke so slurringly of our industry which he chose to ignore the volume of natural dyestuff business was something extraordinary, and to-day after all of the synthetic dyestuffs that have so far been made, and some of which are most excellent and as good as the German colors which they imitate, the volume of the natural dyestuff business is greater than it ever was prior to the world war. In fact, the volume and amount of the natural dyes is becoming a matter of such evident concern to the artificial color people that only in February last a very profound address was made by one of the leading lights of this latter industry in which he stated that he desired to correct a popular impression that the natural dyes were superior to the artificial ones. Unfortunately, not knowing very much about what he was talking he made some rather serious errors, contradicting, in fact, what his own chemist had said last September at the convention of the American Chemical Society in Cleveland, so it looks to us as though it were not entirely improbable that the American manufacturer of artificial dyes had taken a leaf out of the book of the German manufacturer but fortunately not having sunk quite as far down, he does not go at it in such a systematic manner. For that matter we do not feel so fearful about the competition of the

American coal tar dye manufacturers as we did about the German makers for a number of people who were in the habit of using nothing but the artificial dyes, and by this is meant those dyeing concerns which have been in existence for say only the past 20 years or less, a great many of these people had to change to the use of the natural dyestuffs during the war, and a very comfortable percentage of their work is being dyed with natural dyestuffs in direct competition to the artificial products that they formerly had used.

During the period from 1895 to 1914, what I will call the real American dyewood industry held its own, and there is no particular reason why it should not continue to do so for after all the American manufacturers of artificial colors have still to originate one new dyestuff, still to make one dyestuff superior to the German products which they have either imitated or which they have been able through the Alien Enemy Act to take over bodily without work.

As to the quantity of natural dyestuffs used for the 20 years prior to the war from what data I can secure it seems to have averaged about 7,500,000,000 pounds yearly. Since the end of the war, or rather since the Armistice was declared, which may be a little different, the drop in business of all kinds has had a very healthy effect in removing some of the irresponsible people who came into the extract field attracted only by their desire to make immediate money without any idea as to the future of the business, and these are going through a process of elimination, and it will only be a short time before quite a few of these mushroom companies will have vanished, and we trust not to recur again.

Finally in closing it may not be out of place to add that there has been considerable discussion concerning the political phases covering the artificial dyestuff situation. We believe that there should be no antagonism between the producers of the natural dyewood extracts, and the maker of the artificial colors for our interests are naturally bound together, and anything which affects the artificial industry affects ours. If finished dyestuffs are permitted to be dumped into these United States at exceedingly low figures it follows, naturally, that our industry in which there are millions of dollars invested suffers from this foreign invasion.

We have the same thing to face that the American manufacturers of artificial colors have, and that is that when these foreign countries where extract works are now in existence come to the conclusion that they must do everything in their power to circumvent the manufacturers of color, whether it be made from raw material once removed or fifty times removed and whether it comes out of the trees that were growing last year or the coal fields where the trees grew a million years ago makes no difference. What we all have to figure is that in the world's supremacy that our United States now enjoys in dyestuffs, both natural and artificial, there will be a lot of low priced material dumped in here that will have no other redeeming feature than that of price to commend it, and we are just as concerned in having a protective duty placed upon dyes of all descriptions as are our friends, the competition. As far as the quercitron bark extract, flavine and sumac business is concerned, the farmer, the laborer, and the railroads of the United States will alike suffer if our business is harmed for these materials are indigenous to the United States, and the more that the industry can be increased the greater will be the advantage to the American citizen as against the foreign subject. For our part we would be very glad to co-operate in any way which is reasonable and just, and we believe that the time is ripe for some such co-operation on the part of the dye producers of the United States if we wish to protect our industry from the trade onslaughts which are due to recur at any moment.

The result of all this foregoing which has taken a great deal of your time, and possibly without much profit can be summed up in a few words, and those are from one of my friends in the dyewood extract business, "I am sorry that I cannot give you the figures that you ask for, but I think that Mr. Redfield's ridiculous statement that there was no dyestuff industry in this country prior to 1915 can be very readily denied and with tangible proofs."

ABSTRACTS.

Mineral Tannages. *H. and L.*, May 17, 1919. In a recent lecture, M. C. Lamb expressed his opinion that the chrome process was the tannage of the future. The vegetable tannins must be cultivated and years must elapse between the planting of the tree or shrub to yield the tanning material and the maturing to a point sufficient to yield the tanning agent. Mineral tanning agents suffer from no such disadvantage. The great benefit of mineral tannages is that of speed, which (1) enables the market to be more closely followed and watched than by a long vegetable process. (2) Allows a bigger turnover with the same capital or the same plant.

If mineral tannages are cheaper than vegetable tannages and if the resulting leather presents as good appearance or qualities, it will replace the vegetable tannages. Apart from this, however, mineral tanned leather often possess qualities quite distinct from, and for many purposes much superior to, those of vegetable-tanned leather.

The alum tannage, the origin of which is not known, and which is one of the oldest of all processes of converting hide into leather, is a case of mineral tannage. Its old name is that of tawing. It is rarely used alone, that is, as the sole tanning agent. Salt is almost always added, and very often some sort of oil is also used in conjunction with the alum. The alum and salt may also be made into a paste with flour.

With a straight alum and salt tannage, the effect produced may be split up into two parts. The alum in solution hydrolizes to give free acid and a basic salt. The free acid (sulphuric) and the common salt produce together a pickling action as they would do if used without alum. This pickling action produces a kind of leathering effect, and without alum the skin would be more opaque, and if squeezed between the fingers would present a semi-tanned appearance. By this hydrolysis the remaining basic salt produces a true alum tannage. Just as in one-bath chrome tanning a basic salt is needed to produce a permanent tanning effect, with straight alum and salt tanning the basic character of the tanning agent is not very pronounced, but it can be increased very easily by addition of an alkali such as washing soda to the alum and salt solution.

Mr. Lamb emphasized the value of this addition of alkali to the alum, a practice which is not as common as it might be. The washing soda makes the alum tanning agent more basic, which causes the deposition of the alum on the fiber to be not only heavier, but also more firmly fixed, so that the resulting leather is more permanent.

In mineral tannages two main phenomena take place. I. Dehydration of or separation of water from the fibers. II. The coating of the fibers with a basic salt. For any mineral salt to be capable of tanning it must be one giving an insoluble oxide or an insoluble basic salt.

When oil is added to the alum tannage it not only gives softness and body to the leather by coating and lubricating the fibers, but it also produces a tanning effect of its own (a purely oil tannage is, of course, possible—*e. g.*, chamois leather). In the old formulæ for alum tanning

the oil which was added was in the form of egg yolk, which contains about 30 per cent. of an oil similar to olive oil.

The lecturer then gave an historical survey of the two main types of chrome tannage. In 1858 Knapp made experiments on the lines of the modern one-bath process, but did not realize the importance of the process, his resulting leather being, in his opinion, not commercially successful. In 1884 Schultz devised the two-bath process which in many cases is still in vogue to-day, using exactly the same formula as Schultz proposed. In 1890 Martin Dennis patented a one-bath process on the lines of Knapp's early experiments.

The two-bath process is nowadays most largely used for goat skins for glace kid and for sheepskins, while the one-bath process is used for sole leather, calf and side leather. Mr. Lamb was understood to say that he preferred the two-bath over the one-bath process from the point of view of the final leather. The one-bath process has not been developed yet to replace the two-bath process for certain classes of work, such as goatskins for glace kid.

The original Schultz formula was as follows:—For each 100 pounds of pelt, 5 pounds of bichromate of potash, 2½ pounds of commercial hydrochloric acid. The goods are drummed, paddled, or suspended in this until struck through, that is until the yellow color of the chromic acid is even throughout the section. The goods are drained, overnight or longer, and then go into a bath of 10 pounds of hypo and 5 pounds of commercial hydrochloric acid. This treatment may be given in drum, paddle, or by suspension.

The action in the first bath is the liberation of chromic acid by the hydrochloric acid from the bichromate. Bichromate alone will not produce leather. It is essential to liberate the chromic acid from it, either by the acid contained in the pickled goods or by direct addition of hydrochloric acid to the first bath. The amount of acid which should be present or added to the first bath is the amount which is exactly required to liberate the whole of the chromic acid from the bichromate. Very often the amount of hydrochloric acid is much less than this amount, and this means that a proportion of the bichromate is not acted upon and is therefore wasted.

Before the war English tanners almost always used bichromate of potash in preference to bichromate of soda, although the latter has always shown a slight advantage in price. The objection to the soda salt has been its tendency to absorb water, and to become liquid, but this can be avoided by storing in an enclosed space. In certain respects this property is an advantage because it dissolves much more readily.

In the United States some tanners have ceased the use of bichromates, and have turned to chromic acid itself. This plan has the advantage that there is no loss of bichromate unacted upon by the acid.

If bichromate is to be used, the following formula is a common one: For each 100 pounds of pelt, 6 pounds of bichromate of soda, 3 pounds of commercial hydrochloric acid, and 5 pounds of common salt. With

this formula, and with bichromate costing 9d. per pound, the cost of tanning 100 pounds of pelt would be 4s. 10½d., but 3 pounds of hydrochloric acid are only sufficient to liberate the chromic acid from 3¾ pounds of bichromate, so that the remaining bichromate is wasted. If the following formula were adopted, which would give the same results as the one set out above, a considerable economy would be effected:—

3¾ pounds of bichromate of soda.

1¾ pounds of sulphuric acid (equivalent to and to be preferred to 3 pounds hydrochloric acid).

This would cost 2s. 11d. per 100 pounds of pelt, or a saving over the previous common formula of nearly 2s.

Many tanners who use the two-bath process waste enormous quantities of chrome by running away the once-used liquors. In most cases these contain bichromate or chromic acid, and the question arises whether they cannot be used again for making a fresh liquor. These waste liquors can be saved by using them as a preliminary bath. Thus a fresh pack of goods would go into the liquor from which one pack has just been removed, and then into a fresh liquor.

Many tanners of two-bath leathers pickle their pelt in acid and salt before going into the first bath. Its object is to separate the fibers. Previous pickling allows a very good plan to be adopted. By controlling the strength of the pickling bath, the skins can be made to absorb as much acid as is just required to liberate the whole of the chromic acid from the bichromate so that in the first bath no added acid will be necessary. The following plan of pickling allows this principle to be adopted. For each 100 pounds of pelt dissolve 2½ pounds of sulphuric acid and 10 pounds of common salt in 20 gallons of water. Turn the goods in this liquor in the drum for half an hour, then add 6 pounds of bichromate of soda dissolved in a convenient quantity of water. Turn for 3 to 4 hours. By this plan the chromic acid is liberated in situ on the fibers, which is an advantage.

After coming from the first bath, the goods are drained, not exposed to light. The question "How long should goods remain in the yellow condition?" is subject to very different answers. Some say a week, others a few hours. Mr. Lamb thinks that a certain length of time is beneficial, but the time should not be prolonged over two days, because chromic acid is a strong oxidizing agent and the hide fiber is liable to become damaged.

When the goods have been left in the yellow condition covered up for two days they are struck out and placed in the reducing bath containing the hypo and the acid. The acid must not be added too rapidly or the leather might become hard; on the other hand, it must not be added too slowly. The goods are placed in the bath as soon as an opalescence appears. Many goods are spoiled by insufficient hypo. The amount of hypo by the Schultz process (10 per cent.) is not sufficient to reduce the whole of the chromic acid; 15 per cent. is a more suitable quantity. Insufficient hypo will be shown by a brownish color. An economy may be effected by using the hypo baths over again. This is not usually done

because hypo is a comparatively cheap material. By using them over again several times, the amount of hypo may be cut down to 10 per cent. for subsequent packs.

It is an advantage to leave the goods in the reducing bath longer than is necessary to change the yellow to a blue color. It allows sulphur to be deposited, and makes sure that the reduction is complete. If the goods are to be dyed, the reduction may conveniently be started in the morning and paddled until noon, and then left in the spent reducing bath.

A Study of Various Types of Belting. ERNEST D. WILSON, *Shoe and Leather Rep.*, May 8, 1919. Every one who has had experience in the use of belting for power transmission purposes has in a general way decided upon the relative merits of various types of belts and belt materials. He knows that leather can be relied upon to do certain things, and he has a more or less definite understanding of the limitations of other materials. Naturally, since each drive has its own characteristics and difficulties, there is a lack of agreement among the users of belts as to just what the various types of belting will do, and it was to supply this information that the investigation described later was started.

In the course of this investigation power transmission tests were made on two entirely different belt testing machines at different times, and the results obtained check so closely that all data has been combined and incorporated in this report. Tests were made with various types of pulleys, all of which are in every-day use wherever power is transmitted by belting. While different results were obtained with different pulleys, the ratios between the various types of belting materials remained the same. That is, although leather on paper pulleys showed higher results than leather on iron, so also did balata and rubber and the advantage of leather over other materials remained unchanged.

The three essential parts of the belt-testing machine used for conducting these tests are a motor to furnish the power, a generator to furnish the load, and a device to measure the tension of the belt. All machinery is of the most approved and latest type, permitting measurements of the highest accuracy to be taken.

Both motor and generator are direct-current machines and are capable of developing 100 horsepower. They are known as electric dynamometers, and are manufactured by the Sprague Electric Works. The only difference between one of these machines and an ordinary direct-current motor is that the entire field frame is hung on ball bearings so that, when running, the "turning force" which the motor is actually applying to the driving shaft is transferred by levers to a beam-scale, where it can be weighed in pounds. By means of this arrangement for actually measuring the driving force applied to the belt, all theory was eliminated, and the data reported represent purely experimental results.

The power which the belt actually transmitted was measured in the same way by the generator, and the tension under which the belt was running was transferred directly to beam scales and weighed in pounds.

The control panel was equipped so that the speed of the motor could be accurately regulated, and the load applied to the belt by the generator varied throughout a wide range of 0-100 horsepower. The speed was measured by two electrically operated revolution counters.

In all tests the pulleys used were 24 inches in diameter, some were crowned and some straight face. In the series of tests on the first set of machines the belt was run at 3,770 feet per minute, while in the series run on the second set of machines the belt speed was varied from 2,500 to 5,000 feet per minute. Most of the tests were made at 500 revolutions per minute, or a belt speed of 3,140 feet per minute.

As is well known, the tension under which a belt is run determines to a large extent the power which it will transmit. Naturally, it is desirable to keep the tension as low as possible, both to prevent excessive bearing friction and to avoid unnecessary strains on the belt. In conducting comparative tests on various kinds of belts it is necessary to use the same tension throughout. It was found after a large number of trials that the best method of accomplishing this was to start from the same tension, in all cases, when the belt was running at the desired speed under no load. Tests were made at a number of tensions in order to determine whether or not the relative capacities of the belts changed with changing tension. The light running tension varied from 35 to 75 pounds per inch of width, which corresponds to approximately 45 to 90 pounds per inch of width when the belt is standing still. The difference between the tension of the belt standing still and running under no load is due to centrifugal force. Most of the data here presented are based on tests in which the tension was a little higher than that advised by the manufacturers of the various belts, and ranged from 50 to 70 pounds per inch of width when the belt was standing still.

The tests were conducted by increasing the load on the belt from zero to a point where the slip amounted to at least 3 per cent. and the belt showed signs of distress. Measurements of speed, tension, and horsepower were made at each step. The horsepower transmitted by the various belts at different percentages of slips was plotted against slip.

These curves showed that the fabric belts all possessed a very definite maximum beyond which it is impossible to go, and that these points of maximum power-transmitting capacity are below the safe load for leather belting. The leather belts at this speed are rated from 20 to 25 horsepower. The curves showed that leather belting operating at 25 horsepower has an overload capacity of 60 per cent., while not one of the fabric belts, operating with no factor of safety at all, can carry such a load. While it would not be advisable to operate belts at their full capacities, still it is important to know just what margin is available for unforeseen overloads.

A comparison of the various types of belting may be made in another way which takes account of the tension per square inch cross section of the belt. Since the power which a belt will transmit depends directly on the effective tension it will produce this comparison is very valuable.

The point which is of particular interest, however, is that of the safe power transmitting capacities of the different types of belting under discussion. It must be remembered that each of the substitute belts is sold with the statement, and often the guarantee, that inch for inch it is equal if not superior to leather. The enormous advantage of leather is very apparent, and it must not be forgotten that under these ratings the leather belt has an overload capacity of 60 per cent., while the substitutes have practically none.

Since these tests are entirely comparable with ordinary shop and factory practice they indicate the relative merits of these products. It must be thoroughly understood, however, that for any particular drive it is necessary to use the right belt in order for these comparisons to hold true.

TABLE I.

	Rated hp	Total lbs. effective tension	Lbs. effective tension per inch width	Feet per min. to give 1 hp. per inch width	Comparative value leather 100
Leather	25	270	68	490	100
*Solid woven................	16	175	44	760	65
Balata	12	130	33	1,020	49
Friction surface rubber......	10	110	28	1,200	41
Stitched canvas..............	8	86	22	1,500	32

NOTE:—The above figures are safe ratings for the various belts for continuous operation on easy drives; *i. e.,* 180° arc of contact, large pulleys, tight side on the bottom and steady load.

*This refers to the heavy fabric belts, impregnated with gums and oils, and not to the lighter white cotton belts.

CONCLUSIONS.

1. Leather belting possesses a much greater power transmitting capacity than fabric.

2. The enormous advantage of leather over all the substitute belts persists at all speeds up to at least 5,000 feet per minute, and at all tensions within the range practicable for power transmission.

3. The relative capacities of the various belts remain the same on various kinds of pulleys.

4. Leather belting, at its rated horsepower, possesses a big overload capacity, while the fabric belts at much lower horsepower possess no overload capacity whatever.

5. Leather belting improves with age, while the fabric belts are at their best when new.

6. Wherever a fabric belt of a given width is carrying its load with some degree of success, a suitable leather belt three-quarters as wide will do better work than the fabric.

Comparative Value of Different Types of Belting. LOUIS W. ARNY, *Shoe and Leather Rep.*, May 8, 1919. When belts were first used for the transmission of power a century ago, the only material which seems to have been considered was leather, because leather is peculiarly suitable as a material for belting. It has great tensile strength; it is tough, and pliable, and flexible, and it is practically indestructible. It has about it none of the elements of decay, and it is not affected by time. There are in existence pieces of leather that are known to be hundreds of years old, still strong, and full of life. Time has no effect on its chemical construction. Water or dampness does not injure it, and it does not rust, or corrode, or crystallize, or disintegrate. It is injuriously affected only by certain acids, and it wears slowly from the results of friction. A leather belt, properly proportioned to its work and of a suitable character, will render service for a long time with reasonable care. There are in use to-day leather belts which have been running for more than 40 years, transmitting their loads with regularity and having traveled millions of miles, often at the speed of a mile per minute, and because of this long life, the cost of transmitting power by means of leather belting is reduced to a ridiculously small charge per horsepower per annum.

Waterproof leather belts are now made in which the joints are cemented with a material that is not soluble in water, and this belt has the same qualities of durability and permanence for wet conditions as for dry. Water has no effect on either the leather or cement.

The life of a leather belt depends upon the good judgment with which the belt is selected for its work, and the care which it receives. A leather belt requires very little attention in service, but it requires some. It should be clean, and if the ends are not lapped, the lacing or other connection should be kept in order that the ends may be kept perfectly square with each other; any little defects which may develop at the joints should be promptly repaired, and the belt should be dressed occasionally with a good belt dressing, taking care to avoid injurious preparations. Nearly all of the deterioration which occurs in the fiber of the leather can be traced to the injurious character of the dressing, or to the excessive quantities which have been used. Abuse and neglect are, therefore, the principal enemies of the leather belt, and where these are eliminated a long life may be expected from any suitable leather belt on a well designed drive.

When it has become an old belt, and is beyond the repairing ability of the mechanic of the shop, it can be rebuilt by its maker, the bad places cut out, the good detained, and sufficient new added to make the proper length. It is then good for many more years of usefulness. Or, if there is no place for it in the shop which has owned it, there is a ready market for it as a second-hand belt at a good price. When, in its extreme old age, repairs become inadvisable, it still has a value for use in repairing other old belts, or for straps, brake shoes, heel taps, etc. The last remnant of it is worth something to somebody.

It will be observed that none of these statements are true of those belts which are used as substitutes for leather belts. Experience has demonstrated that even under the smaller loads of which they are capable their lives are but a small fraction of that of the leather belt; they cannot be made endless in a practical way, and when so made the joints cannot be opened and cemented together again by the shop mechanic. These ends then must be joined by metallic or leather fastenings, which are not permanent, and which soon destroy the fabric of the ends of the belts, so that it usually becomes necessary to insert other pieces of the belt to make the length, doubling the number of joints and the probability of trouble from them. These belts cannot be run where the belt may be chafed on the edges, and they cannot be cut down into other sizes, or repaired or rebuilt, and when they finally are discarded, they have no salvage value, but must be cast upon the dump.

Some of these belts have a low cost; others of them approximate the cost of the leather belt, but all of them, calculated on a basis of the cost of transmission per horsepower per annum, will be found to cost many times the price of the best leather belts.

Analysis of Artificial Leather and Leather Substitutes. R. LAUFFMANN, *Z. öffentl. Chem.*, 24, 212-220, 239-240 (1918); *J. S. C. I.*, 38, 227A (1919). The base of artificial leather usually consists of animal fibers (hide, muscle, or wool) either raw or tanned, vegetable fibers, and cellulose, formed into sheets by the aid of such binding materials as caoutchouc, guttapercha, glue, casein, dextrin, starch, resins, tar, etc., varnishes, cellulose esters, and viscose. Oils, particularly castor oil, are added to render the material pliable, and the following are used as fillers:—Aluminium compounds, antimony sulphide, lead oxide, ochre, zinc oxide, zinc sulphate, calcium carbonate, calcium chloride, sodium silicate, cement, and various pigments. A microscopical examination of the material before and after treatment with water and solvents will give some indication of the character of the substances present. The procedure given below is suggested for the chemical analysis of the material; in many cases, it is almost impossible to isolate the various constituents, but these may be separated into groups which may be examined by the usual methods to ascertain, as far as possible, the nature of the components. A. The finely-divided material is extracted thoroughly with ether and petroleum spirit; fatty oils, paraffins, rosin oil, resin, waxes, portions of incompletely sulphonated oils, and certain portions of caoutchouc and guttapercha are dissolved. B. The insoluble residue from A is extracted with cold water and then with hot water; the aqueous extract will contain glue, gelatine, albumin, casein, starch, dextrin, gum, tannin, glycerol, alkali soaps of normal and oxidized fatty acids, resin acids and soluble mineral substances. C. The insoluble residue from B is warmed with dilute hydrochloric acid and then extracted with ether; the ethereal solution will contain the fatty and resin acids of soaps that were insoluble in water, and the aqueous acid extract the bases of these soaps together with other

mineral substances. D. The residue from C is extracted with acetone; nitro cellulose and acetyl cellulose pass into solution probably contaminated with soluble portions of caoutchouc, etc. E. The residue from D is dried and the nitrogen is determined in a portion of it; if nitrogen is absent, the material does not contain animal fibers or leather. The residue is then boiled with alcoholic potassium hydroxide solution; oxidized fatty acids, resins from varnishes, sulphonated oils and animal and vegetable substances are dissolved. F. The insoluble residue from E is extracted with pyridine to dissolve tar, pitch, and asphalt; portions of caoutchouc and guttapercha also go into solution. G. The residue from F is extracted with toluene; caoutchouc and guttapercha are dissolved. The final insoluble residue consists of vegetable fibers, cellulose and mineral substances. The total mineral substances should be determined and identified in the ash of the original material.

Method of Determining Free Sulphuric Acid in Leather. C. IMMERHEISER, *Ledertechn Rundsch.*, 10, 81 and 86 (1918); *Chem. Zentr. II.*, 75 (1919); *J. S. C. I.*, 38, 227A (1919). The ordinary method of determining free sulphuric acid in leather is not applicable to leather which has been tanned with materials containing sulphited tannin extracts, sulphite-cellulose extract, etc. In such cases 10 grams of the leather is extracted three times for 12 hours each time with 200 cc. of water at the ordinary temperature, and the united extracts are exaporated with 5 grams of quartz sand on the water-bath. The dry residue is powdered and treated in a stoppered flask for about 2 hours with 100 cc. of anhydrous ether, the flask being meanwhile occasionally shaken. The ethereal extract is filtered and the leather again twice extracted with 40 cc. of anhydrous ether. The united extracts are treated with hydrochloric acid and barium chloride, the ether distilled, and the residue evaporated to dryness on the water-bath in order to decompose the ethylsulphuric acid. The dry residue is treated with 50 cc. of hot water acidified with hydrochloric acid, allowed to settle, the liquid filtered, and the barium sulphate determined in the usual way. The sulphuric acid thus determined is present in the leather in the free state. The combined sulphuric acid present in the form of soluble sulphates may be determined in the residue from the extraction with ether.

Vegetable Dyes in Japan. *Brit. Board of Trade Jour.*, Jan. 9, 1919. The British Consul at Shimonoseki reports that some sixty varieties of trees and twelve varieties of plants have been found to possess value as dyestuff materials. The principal of these are given as follows: *Pinus densiflora* (Aka-matsu), found throughout Japan in the wild state; the leaves give a dark brown dye used for cotton yarn. *Pinus Thunbergii* (Kuro-matsu), is a common variety of pine and gives a dark brown dye which is extracted as follows: 10 parts of the fresh leaves are mixed with 3.3 parts of sulphur and 10 parts of sodium sulphide and heated with water for 5 hours. It is easy to recognize in this the preparation

of a brown sulphur dye; it is said the dyestuff so formed commands a ready sale. *Chestnut* (Kuri); the bark is used treated with copper sulphide and gives a brown dye much in use for saddlery wares; while the leaves and bark also yield a black dye for silk (no doubt in connection with an iron salt—the "black dye" being really tannin); the roots furthermore give a yellow dye used for the staining of furniture. *Quercus dentata* (Kashiwa), a variety of oak; a decoction of the bark gives a material used for dyeing hemp, cotton, etc., a khaki color. *Quercus serrata* (Kunugi); the fermented leaves give both brown and dark green coloring matters. *Pomegranate* (Zakuro); the bark gives a dye employed in leather dyeing. *Pasania cuspidata* (Shii) gives a dyestuff used on fishing nets. *Camellia Japonica* (Tsuboki); the leaves when pressed give a green coloring matter used for the dyeing of cheap mosquito nets. *Myraca rubra* (Yamaroma); the juice extracted from the leaves and bark furnishes a dye for fishing nets, also used as a bottom for indigo dyeing, and for the dyeing of khaki uniform cloth.

Tanning With Iron Salts. DR. V. CASABURI. (*Reale Istituto D'Incoraggiamento Di Napoli.*) Abst. *The Leather World,* May 15, 1919. Of the various substances used to convert pelt into leather, iron salts have, from time to time, attracted a certain amount of attention. Ashton in 1794 used oxide of iron in conjunction with sulphuric acid. This was improved upon in 1842 by Bordier, who tanned with a basic iron salt. Knapp also investigated the process (1861) and Eitner in 1881 used a combined iron and chrome tannage. Reinsch in 1892 suggested the addition of salt to the iron chloride, and afterwards (1912) used an iron tanning solution made with iron chloride, magnesium carbonate and chloride of aluminium. Bystron and Vietinghoff (1911) patented the process of using iron sulphate oxidized to ferric sulphate by oxides of nitrogen. The author has made experiments with various iron salts with results given below.

Basic ferric sulphate was prepared by dissolving 166.8 grams of sulphate of iron in 1.2 liters of water, and adding 37.7 grams of 60° Bé H_2SO_4 and 18.5 grams of 42° Bé HNO_3. Soda was then added to form the salt $Fe_2(SO_4)_2(OH)_2$ and the gravity made 1.110.

Six molecular proportions of ferrous sulphate, and 6 molecular proportions of HCl were treated with two molecular proportions of HNO_3. The solution was then made basic by adding one molecular quantity of Na_2CO_3. 100 cc. of the liquor contained 4.93 grams Fe_2O_3 and 7.91 grams H_2SO_4, the basicity being

$$Fe_2O_3 : H_2SO_4 : : 100 : 159.$$

Metallic iron was dissolved in HCl and the solution oxidized by nitric acid according to the equations—

$$Fe + 2HCl = FeCl_2 + H_2.$$
$$6FeCl_2 + 6HCl + 2HNO_3 = 6FeCl_3 + 4H_2O + 2NO.$$

Soda was then added to make the iron salt basic to the extent of $Fe_2Cl_4(OH)_2$.

Ferric acetate was made by oxidizing 166.8 grams of ferrous sulphate in solution with 37.7 grams 60° Bé H_2SO_4, with 18.5 grams of 40° Bé HNO_3. The calculated amount of lead acetate to make ferric acetate was then added, and the insoluble lead sulphate filtered off.

Pelt was tanned with solutions of the above iron salts, and the amount of iron fixed in the finished product was equivalent to from 7.1 per cent. to 7.88 per cent. of Fe_2O_3. During tanning the variation in basicity of the liquor was ascertained by titrating the acid by the Proctor-McCandlish method (as used for chrome liquors), and estimating the iron volumetrically. The ratio $Fe_2O_3 : H_2SO_4 :: 100 : x$ was then calculated.

Pelt was tanned with the basic ferric sulphate with an addition of salt to the liquor. Tanning was commenced in a 1° Bé liquor, which was gradually strengthened to 4° Bé. The leather was then dipped in a 5° Bé solution of sulphate of soda, and finally in running water. The finished leather was analyzed, with the following results:—

Moisture, 23.34 per cent.; fat, 0.89 per cent.; total ash, 6.69 per cent.; Fe_2O_3, 6.17 per cent.; water soluble matter, 3.7 per cent.; ash of water solubles, 2.8 per cent.; hide substance, 68.3 per cent.

Oils and Greases in the Leather Industry. *Les Matieres Grasses*, 131, 5066 (1919). ANON. From the earliest times, oils and greases have been a necessary adjunct to the art of the tanner and leather dresser. In fact tanning with oils is one of the most ancient methods of preserving hides. It is still used by the Indians of North America, and the rugs of buffalo hides tanned and dressed by the squaws are among the best specimens of flexible leather extant. The procedure is simple and depends upon the docility of the squaw, upon her strength, patience and good disposition. The skin is first stretched, then scoured, given a drubbing with fat and stretched several times during the process of drying. This, however, is a progress upon the methods employed by the Esquimaux. The women render flexible and tan the skins of the seal and other animals by chewing on them with their teeth and an authority on the country states that it is wholly current to see women whose teeth have been worn completely by this hard form of dental exercise.

The old Boers of South Africa fabricated a very good leather called "reim leather," they cut the fresh hide in strips, suspended them from a beam and oiled and twisted them continually as fast as they dried. The "reims" are very resistant and durable and are much used as a kind of crude harness for the teams of oxen. In fact, every true Boer carried somewhere about him coils of "reim leather" carefully attached to his equipment because his very existence depended on the successful mending of his harness when he had such great distances to travel.

It is seen that tanning with oil has always been practiced under some form or other by primitive people and it is curious to observe, in spite of all of our progress in chemistry, that method of preparing leather is

still in vogue. Chamois and analogous leathers are prepared by working with fish oils, and by this process, by allowing to heat in piles and with the subsequent oxidation, a leather is obtained that is resistant to putrefaction and employed in a great many well known ways.

We now come to the use of greases and oils on leather tanned by other methods, including the old vegetable process and the more modern process with chromic oxide. Formerly tallow appeared to have been considered by experts as the best product for rendering tanned leather flexible and impermeable to water. Still human nature seems to have always been disposed toward offering something better (in lieu of superior profits), in fact one sees many of the old laws containing references relative to the penalties decreed for the substitution of various substances for good tallow. A study of the old statutes of England shows that a severe control has been exercised over the hide industry, the tannery and the curriery. Penalties have been indicated for hides that have been cut or gashed or watered, for leather insufficiently tanned, etc. It seems that the introduction of female labor in the leather manufactories is not an innovation in that country, since one of the statutes declare that "no one is allowed to be a tanner without having served 7 years, except the wife or a son of a tanner having 4 years of practice, or the son or daughter of a tanner, or a person marrying a wife or daughter to whom the tanner has left an installation, under penalty of confiscation of all the leather tanned by them." Of that which concerns the use of greases for the curriery, the currier was severely punished if the leather was not curried within a determined lapse of time. He must not use old urine nor other fallacious substances that would destroy the hide; nor to curry sole leather with a material other than hard tallow, nor with less of tallow than the leather would absorb.

The times have well changed since the time of James I. Science has entered into the manufacture of leather and with that the fraud of many of the products used has passed. The author remembers how, formerly, leather for shoes, harness and saddlery was treated with a very good mixture of tallow and cod oil known under the name of "dubbin." This mixture was applied in the semi-fluid state to the wet leather, the fatty material penetrating into the fiber of the leather as the water evaporated. The resulting product was a flexible leather, excellent for long usage. Later the method of drumming, coming from America, was introduced. This consisted of working the nearly dry leather in a large drum to saturate them with the hot, melted greases. As the more solid greases are absorbed by leather better than tallow, it is possible to use freely such material as stearine, mineral waxes, etc. The leather obtained is cheaper and plumper and it is preferred by the consumer who considers the lower price rather than superior quality.

With the more modern chrome leathers—and to a certain degree with products of a vegetable tannage—lubrication is accomplished more or less by saturating the leather with emulsions of different oils. Neatsfoot oil perhaps gives the ideal emulsion, with addition of a little egg

yolk, moreover, it is nearly impossible to obtain a product as good. We curriers are obliged to be content with sulphonated oils and prepared fat liquors that give better results than with hand dressing.

Before the war, very little attention was given, in the leather industry, to the recovery of grease. In many cases the curriers who employed the old hand process lost considerable grease. A large amount of grease and oil was either thrown away or sold at a low price to firms who used it and who after having purified the grease obtained, frequently resold the hard greases to the curriers under a special name.

In ending the author mentions a new experience, the treatment of the human skin with paraffin, which is in full progress in the Great Northern Hospital, Becketts Park, Leeds. The proprietor of a tannery at Churwell, having read some time ago that a French physician used melted paraffin in the treatment of rheumatism and for troubles of the circulation, proposed, in his position as a large consumer of that material, that a similar bath might be installed in his establishment. He installed a bath and treated gratuitously at the tannery about one hundred cases. But when orthopedic treatment became very important for the disabled soldiers, he removed his bath to the place indicated above. Contributions from the leather industries enabled American physicians to install another bath in another hospital. It seems, therefore, that that bizarre evolution, derived from the treatment of leather, contributed to diminish the sufferings of humanity. G. W. S.

Journal of the

American Leather Chemists Association

Vol- XIV | AUGUST, 1919 | No. 8

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Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $6.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized July 16, 1918.

PROPOSAL TO CHANGE SECTION 8 OF THE BY-LAWS OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION TO READ AS FOLLOWS:

8. Every candidate for admission to active membership must have the following qualifications: (1) ability to execute properly all analytic methods of the Association; (2) knowledge of the chemistry upon which these methods are based. No special qualifications are required of candidates for associate membership other than an interest in the Association and its work.

Each application for membership shall be made upon a copy of Form No. 1 given below, which must be signed by at least two active members who shall declare themselves satisfied that the candidate possesses the qualifications requisite for the kind of membership for which application has been made.

FORM NO. 1.

THE AMERICAN LEATHER CHEMISTS ASSOCIATION.

We, the undersigned active members of this Association, hereby propose (candidate's name in full).............................as a fit and proper person to become a (write active or associate as needed).......... member of this Association and declare that we are fully satisfied that he possesses all qualifications requisite for (write active or associate as needed)...........membership.

Proposed by...
....
....

And I, the said candidate, declare that I possess the qualifications requisite for (write active or associate as needed)..........membership and, if elected, will do my best to support the Association and will observe its By-Laws.

Signature of candidate...................................
Address ....
Occupation ....
Firm name and address..................................

NOTE: This application is to be accompanied by the candidate's written statement of schools he has attended, degrees obtained, positions held, with length of service, and general experience, so that the Council may use it as a guide in determining the eligibility of the candidate.

The application, properly filled out, must be sent to the Secretary, who shall lay the same before the Council. If a majority of the Council is in favor of his election, the candidate shall be declared duly elected, and his name entered in the register of the Association.

If the candidate's application is rejected by the Council and all members who signed said application believe that the Council acted unwisely, they may, by securing the signatures of a total

of ten active members and submitting the same to the Secretary on a copy of Form No. 2 given below, cause the candidate's application to be submitted to a mail vote of the entire Association.

FORM NO. 2.

THE AMERICAN LEATHER CHEMISTS ASSOCIATION.

We, the undersigned active members of this Association, are of the opinion that the Council may have acted hastily or unwisely in rejecting the application of (candidate's name in full).......................... for (write active or associate as needed)................membership and hereby request that said application be submitted to a mail vote of the entire Association.

1. ....
2. ....
3. ....
4. ....
5. ....
6. ....
7. ....
8. ....
9. ....
10. ....

At any time within sixty days after receipt of this request, the Secretary shall submit said application to a mail vote of the entire Association, If a majority of those voting is in favor of his election, the candidate shall be declared duly elected. and his name entered in the register of the Association. If the candidate's application be again rejected, he shall not be allowed to present another application for membership until eighteen months have elapsed since the taking of the mail vote, unless the Council by special vote should shorten this period.

At whatever period of the year a new member may be elected, he shall be required (unless the Council determines otherwise) to pay his dues for that year.

Proposal made by JOHN ARTHUR WILSON.
Seconded by ERWIN J. KERN.

THE EXTRACTION OF GREASE AND OIL FROM LEATHER—COMMITTEE NOTICE.

By John Arthur Wilson, Chairman.

The action of the Council in tabling the proposal[1] of the 1918-1919 Committee that chloroform be adopted as the official solvent for determining oils, fats, and waxes in leather would seem to indicate that the Committee had been over hasty in its recommendation. That is a matter of viewpoint which may be allowed to rest; the moot point is that the Committee is expected to produce a second report before one of its proposals may be submitted to a vote.

Last year the Committee worked on what seemed the most likely plan to determine the relative efficiencies of five common solvents in extracting oils, fats, and waxes from leather and completed all of the work undertaken, making nearly two thousand separate determinations, all of which indicated that chloroform is the most and petrol the least efficient of the five solvents. The writer believes that any question raised against this conclusion must be considered rather against the plan which the Committee employed. It is easy to question any work; it is more indicative of real interest to suggest how it could have been done better. As yet no plan better than that employed last year has been offered.

The work is not complete; it probably never will be. If last year's plan had been completely acceptable, we might have gone on examining other solvents, but we can hardly afford the time to do this with a questionable method. Every sufficiently interested person is requested to send in as soon as possible a practical outline of work for the coming year. One suggestion was to analyze various kinds of finished leathers and then to determine the amounts of foreign matters extracted with the fats. This was the first method considered last year, but we found ourselves

[1] Two proposals were made, one to change an official method and one to *add* to the provisional methods. The Council evidently overlooked the fact that the latter proposal does not come under its jurisdiction; according to Section 23 of the By-Laws, the Secretary "shall immediately submit it to a mail vote of the active members of the Association." The results of this vote, which we hope will now soon be taken, will aid the Committee in planning work for the coming year.

unable to make thorough quantitative analyses of the fat extracts that could in any way be considered satisfactory. It would be simple enough to determine most of the inorganic constituents, but we were floored by the organic ones. But, it is possible that someone may find a better method than we did to overcome this difficulty. Kindly send all suggestions to the writer, care of A. F. Gallun & Sons Co., Milwaukee, Wis.

COUNCIL MEETING.

A meeting of the Council was held Friday, June 13 at the Chemists Club, New York, all members being present.

COMMITTEES.

The Secretary was instructed to prepare a circular letter giving the committees and the chairman of each. This is to be sent to all the active members requesting them to signify which committee or committees they desire to serve on and return the notice to the Secretary who will then advise the chairman of each committee of those who desire to work on his committee.

Extraction of Grease and Oil from Leather.

This Committee was continued with John Arthur Wilson as chairman.

Determination of Total, Soluble and Insoluble Ash in Leather.

J. M. Seltzer, chairman. No further experimental work is asked of this Committee but it is requested to draw up a definition of total and insoluble ash and submit it to the Council.

Committee for the Standardization of Kaolin.

This Committee has for its object to obtain a uniform supply of kaolin which shall be tested by the members of the committee, W. K. Alsop, chairman; H. C. Reed, J. S. Rogers, C. R. Oberfell and T. A. Faust.

Sulphite Cellulose in Synthetic Tans, Tanning Extracts and Leathers.

This Committee was discontinued.

Sulphonated Oil Analysis.

Continued with G. W. Schultz, chairman.

Methods of Leather Analysis.

A Committee consisting of W. K. Alsop, J. B. Churchill and H. C. Reed was appointed to revise the official method for sampling and analyzing leathers with authority to appoint such sub-committees as may be desired. This Committee was also instructed to work out its plan of procedure so that the Secretary may include on his statement in reference to committees a list of the sub-committees.

Determination of Free Sulphuric Acid in Leather.

A resolution was passed requesting J. B. Churchill, chairman of the committee last year to submit the Procter-Searle method as modified in his report in proper form to be adopted as a provisional method, also that he be requested to continue any committee work he may deem advisable.

Standardization of Lime for Tannery Use.

Committee consisting of Mr. Smoot, Dr. Levi, Guy T. Creese to collaborate with the American Society for Testing Materials with a view of arriving at a standardization of lime for tannery use.

Two proposals for changes in the methods[1] submitted by John Arthur Wilson were discussed at some length and a resolution was passed that these proposals be tabled for the time and that the Council await the report of this year's committee before taking action.

Proposal to change the provisional methods of the Association for the analysis of one bath chrome liquors.[2]

Before acting on this the Council thought it desirable to have the Secretary take up the matter with the Society of Leather Trades Chemists with a view of arriving at a common mode of expression for the subject involved.

After considerable discussion of the subject a motion was passed that a letter be sent to every active member of the Association stating that there has been some criticism of the Association because of its failure to undertake problems of practical interest to the tanner, and requesting that each member reply to

[1] This JOURNAL, 14, 234.

[2] Ibid. 14, 235.

the letter, stating any problem which he thinks is suitable for treatment by the Association, giving his idea as to how it may be handled by the Association and including a practical means of attack on the problem.

A resolution was passed increasing the remuneration of the Secretary's assistant to $450 per year and that of the Associate Editor to $250 per year.

THE EFFECT OF THE CONCENTRATION OF A CHROME LIQUOR UPON ADSORPTION BY HIDE SUBSTANCE.*

By Mabel E. Baldwin.

The present investigation was made in pursuance of the research which has been carried on in this laboratory during the past 2 years in the field of leather chemistry. A study has been made of the acidity of chrome liquors and the changes in acidity caused by the addition of certain electrolytes.[1] While this work is being continued it was thought desirable to carry on simultaneously a study of the chrome-tanning process.

In the process of chrome tanning there are many variable conditions involved, such as the concentration of chromium in the chrome liquor, length of time during which the hide substance and liquor are in contact, temperature at which the tanning takes place, concentration of hydrogen ion in the liquor, and kind and amount of neutral electrolyte present. In a thorough study of the process each one of these factors must be considered separately and will be taken up as rapidly as time permits.

The concentration factor, that is, the effect of the concentration of the chrome liquor upon the adsorption by hide substance of the constituents of the liquor is the first factor studied and the results are recorded in the tables which follow.

*Read at the Annual Meeting of the A. L. C. A. at Atlantic City, May 23, 1919.

[1] The Acidity of Chrome Liquors, by A. W. Thomas and M. E. Baldwin, This JOURNAL 13, 192 (1918).

The Action of Neutral Salts Upon Chrome Liquors, by A. W. Thomas and M. E. Baldwin, This JOURNAL 13, 248 (1918).

The Action of Neutral Chlorides Upon Chromic Chloride Solutions, by M. E. Baldwin, This JOURNAL 14, 10 (1919).

According to the general plan of the experimental work, a series of solutions containing varying amounts of a stock chrome liquor were made and to each was added a definite amount of hide substance. After equilibrium was reached an analysis was made of the chromed hide substance and the amount of chromium and of sulphate removed from the liquor was measured by determining the concentration of these constituents before and after adsorption. In recording the results chromium is calculated as chromium oxide, Cr_2O_3, and sulphate as sulphuric anhydride, SO_3.

Experimental.

Chrome liquor.—

The chrome liquor used was a stock liquor of the following composition:

Cr_2O_3	215.0 grams per liter.
SO_3	219.0
Fe_2O_3	30.9
Al_2O_3	3.2
NaCl	6.5
Glucose	none
Specific gravity	1.625 at 27°C.
Basicity corresponding to Cr (OH)	1.06 (SO_4) 0.97

Hide powder (American Standard).—

An analysis of the hide powder gave the following results:

Moisture	10.92 per cent.
Ash	0.44
Protein (N $\times$ 5.614)	88.78

Procedure.—

The stock chrome liquor was diluted with increasing amounts of distilled water to make a series of solutions in which the concentrations of Cr_2O_3 ranged from 6.5 to 0.04 gram per 100 cc. Two hundred cubic centimeters of each of these solutions were poured upon 5-gram portions of hide substance contained in glass-stoppered bottles. These mixtures were kept at room temperature (approximately 22° C.) and were shaken at intervals for 48 hours. At the end of this period each mixture was filtered by suction on a dry Buchner funnel, the filtrate set aside for analysis, and the chromed-hide powder was then washed with distilled

water until the wash water was free from sulphate. The chromed-hide powder was dried at 40°C, then at 100°C, until free from moisture. It was found necessary to dry the hide powder in two stages because it gelatinizes if placed in the 100° oven while it still contains much moisture. The chromed-hide powder was analyzed for protein, ash, chromium, and sulphate. Chromium was determined in the ash after heating with a mixture of two parts MgO and one part Na_2CO_3. Sulphate was determined by precipitation of $BaSO_4$ after fusion of the chromed-hide powder with Na_2O_2 and acidifying.

Both of these determinations were made on portions of each of the solutions before and after adsorption.

Measurements were also made to determine the change in hydrogen ion concentration of the liquors caused by the removal of constituents during adsorption. Since, as has been previously shown,[2] there is a slow change going on in the liquor for some time after dilution, the experiment was so arranged as to exclude the possibility of attributing this change to adsorption by the hide substance. This was done by allowing a portion of each of the original solutions to stand two days, then determining the concentration of hydrogen ion in these solutions at the same time as in the filtrate. The difference in concentration of hydrogen ion in these solutions may be attributed to the presence of the hide powder.

Results.

The results for analysis of the chromed-hide substance are given in Table I. Having analyzed the chromed-hide substance for Cr_2O_3, SO_3, and protein, the results should total 100 per cent. or nearly so. From the figures it is seen that a small amount, less than 2 per cent. in all cases, is still undetermined. Some of this is the ash of the original hide powder and some is probably due to the variation of the protein factor, 5.614, because of changes in the nature of the collagen during the tanning process. A comparison of the weight of the ash with that of Cr_2O_3 shows that the ash is made up almost entirely of Cr_2O_3 although a small part of the sulphate is left with the ash.

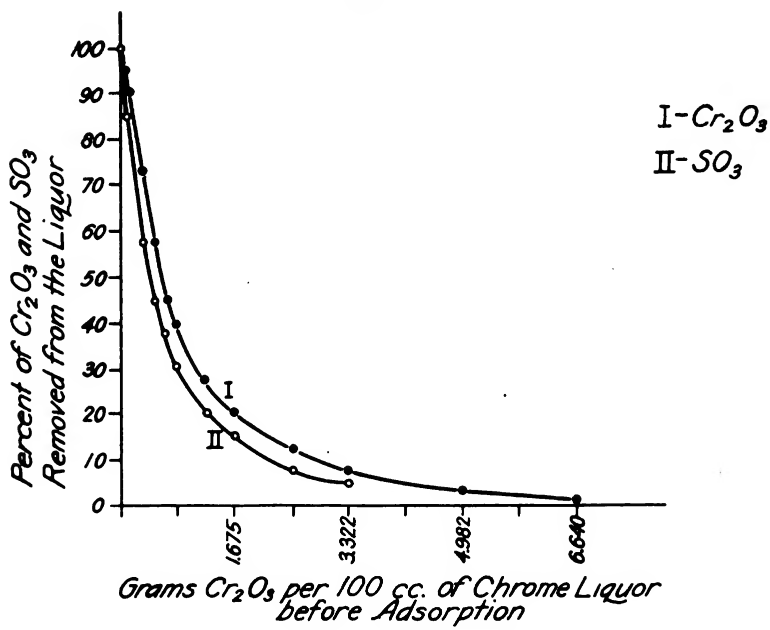
[2] Thomas and Baldwin, l. c.

TABLE I.—THE RELATION BETWEEN THE CONCENTRATION OF THE CHROME LIQUOR AND THE COMPOSITION OF THE CHROMED-HIDE SUBSTANCE.

Number of solution	Gm. Cr_2O_3 per 100 cc. of liquor before adsorption	Composition of the chromed-hide substance: Per cent. protein	Per cent. Cr_2O_3	Per cent. SO_3	Chromed-hide substance per cent. ash
1......	0.038	97.0	1.3	1.6	1.5
2......	0.079	91.0	2.7	3.3	3.1
3......	0.165	88.0	5.1	6.0	5.6
4......	0.328	84.2	7.8	7.6	8.3
5......	0.493	82.0	9.1	8.4	9.7
6......	0.660	81.0	9.6	8.8	10.5
7......	0.815	79.0	9.9	9.1	10.8
8......	1.232	78.1	10.3	9.6	11.2
9......	1.675	78.0	10.4	9.7	11.4
10......	2.509	78.3	10.3	10.1	11.1
11......	3.322	79.1	9.8	10.3	10.8
12......	4.982	80.0	9.3	10.6	10.1
13......	6.640	80.8	7.6	10.8	8.9

The results of the measurements of the change in concentration of Cr_2O_3 and SO_3 in the liquors during adsorption are given in Tables II and III. A comparison of the concentrations before

Figure I



and after adsorption shows the per cent. of the constituents which is removed from each solution by the hide powder. As is most

easily seen when these results are expressed in the form of curves, Fig. 1, the percentage removed from solution decreases very rapidly as the concentration of the liquor increases. For example, in the case of chromium oxide, at a concentration of 0.08 gram Cr_2O_3 per 100 cc., the liquor gives up to the hide powder 95 per cent. of its chromium content, while at 0.66 gram

TABLE II.—THE CHANGE IN CHROMIUM CONTENT OF THE LIQUOR DURING ADSORPTION.

Number of solution	Concentration of chromium oxide in the chrome liquor: Gm. Cr_2O_3 per 100 cc. before adsorption	Gm. Cr_2O_3 per 100 cc. after adsorption	Grams Cr_2O_3 removed from 100 cc.	Per cent. Cr_2O_3 removed
1......	0.038	0.001	0.037	96.3
2......	0.079	0.003	0.076	96.2
3......	0.165	0.014	0.151	91.4
4......	0.328	0.089	0.239	73.8
5......	0.493	0.203	0.290	56.9
6......	0.660	0.346	0.314	44.7
7......	0.815	0.485	0.330	39.2
8......	1.232	0.892	0.340	27.1
9......	1.675	1.335	0.340	20.2
10......	2.509	2.206	0.303	12.4
11......	3.322	3.072	0.250	7.4
12......	4.982	4.844	0.138	2.8
13......	6.640	6.620	0.020	1.4

TABLE III.—THE CHANGE IN SULPHATE CONTENT OF THE LIQUOR DURING ADSORPTION.

Number of solution	Concentration of sulphate in the chrome liquor: Gm. SO_3 per 100 cc. before adsorption	Gm. SO_3 per 100 cc. after adsorption	Grams SO_3 removed from 100 cc.	Per cent. SO_3 removed
1......	0.0387	0.0015	0.0372	96.1
2......	0.0804	0.0117	0.0687	85.4
3......	0.1680	0.0567	0.1113	66.3
4......	0.3341	0.1428	0.1913	57.3
5......	0.5020	0.2787	0.2233	44.5
6......	0.6720	0.4163	0.2557	38.1
7......	0.8301	0.5699	0.2602	31.3
8......	1.2550	1.0000	0.2550	20.3
9......	1.7060	1.4617	0.2443	14.3
10......	2.5560	2.3525	0.2035	8.0
11......	3.4300	3.2700	0.1600	4.7

per 100 cc. only 45 per cent. is given up. The percentage adsorbed is very low in the more concentrated liquors, being less than 3 per cent. at a concentration of 5 grams per 100 cc. At the

point of maximum adsorption 20 per cent. of the chromium is removed from the liquor. In the case of the sulphate constituent of the liquors the results are similar, but in every case, the percentage of sulphate removed is less than that of chromium.

When the amounts of chromium and sulphate adsorbed per unit weight of hide substance are calculated from the results given in Tables I, II, and III, the values in Table IV are obtained. These results are expressed more clearly perhaps by the curves in Figs. 2 and 3.

TABLE IV.—THE AMOUNT OF Cr_2O_3 AND SO_3 ADSORBED BY UNIT WEIGHT OF HIDE SUBSTANCE.

Number of solution	Mg. of Cr_2O_3 adsorbed by 1 gram of hide substance: Calculated from analysis of chromed-hide substance	Mg. of Cr_2O_3 adsorbed by 1 gram of hide substance: Calculated from analysis of liquors before and after adsorption	Mg. of SO_3 adsorbed by 1 gram of hide substance: Calculated from analysis of chromed-hide substance	Mg. of SO_3 adsorbed by 1 gram of hide substance: Calculated from analysis of liquors before and after adsorption
1	13	16	17	15
2	30	30	36	27
3	57	60	68	45
4	94	96	90	76
5	110	116	102	89
6	118	126	109	102
7	125	132	115	104
8	132	136	123	102
9	134	136	124	98
10	131	120	129	81
11	125	100	130	64
12	116	55	132	——
13	103	8	133	——

Curve I, Fig. 2, represents the amount of Cr_2O_3 remaining with the hide substance after it is washed free from soluble matter, then dried. This curve shows the maximum amount of chromium is adsorbed when the liquor contains from 1.5 to 2 grams Cr_2O_3 per 100 cc. At this concentration the amount of Cr_2O_3 remaining with 1 gram of hide substance amounts to 134 milligrams. A further increase in the concentration of the chrome liquor causes a slight decrease in the amount of chromium adsorbed. At concentrations less than that causing maximum adsorption the amount of Cr_2O_3 in the chromed-hide substance is less as the concentration of the liquor decreases.

Assuming that the change in chromium content of the liquors

Figure II

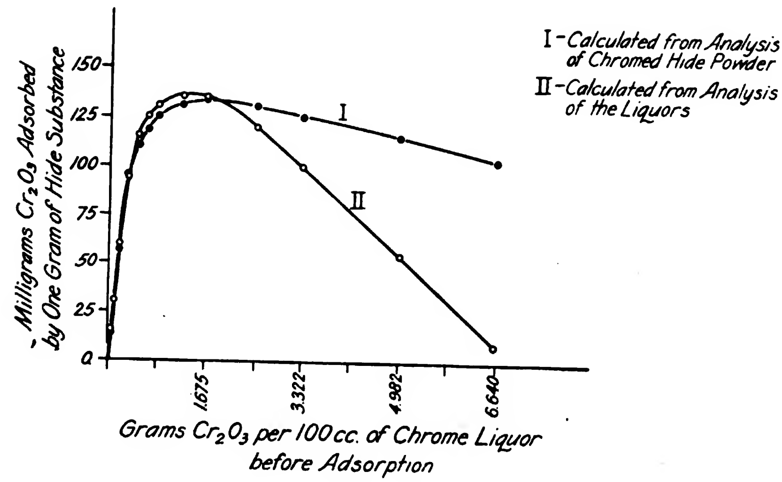
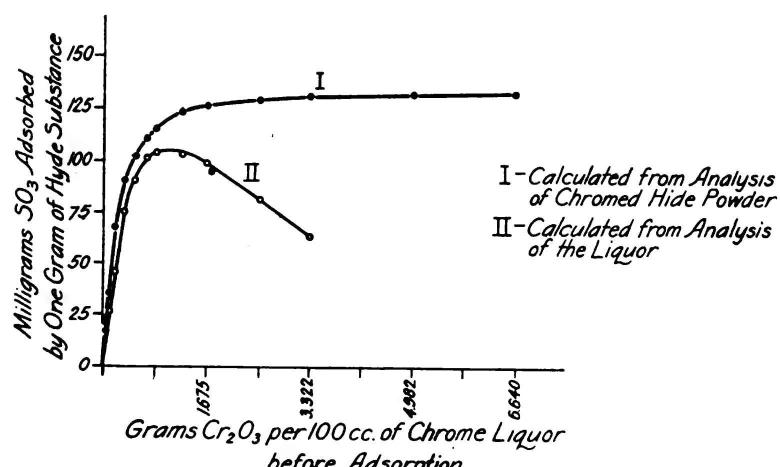


Figure III



during adsorption may be used as a measure of the amount of chromium adsorbed by the hide powder, these values were cal-

culated and are given in Table IV. They are also graphically represented by Curve II, Fig. 2. Both of these curves in Fig. 2 have their maximum in the same place but comparison shows that analysis of the liquors before and after adsorption is not a true measure of the amount of chromium or sulphate adsorbed by the hide powder.

The values for sulphate were similarly calculated and are expressed in Table IV and Curve II of Fig. 3.

The measurements of hydrogen ion concentrations in the liquors are given in Table V and Fig. 4.

TABLE V.—THE CHANGE IN THE HYDROGEN ION CONCENTRATIONS OF THE CHROME LIQUORS DUE TO ADSORPTION.

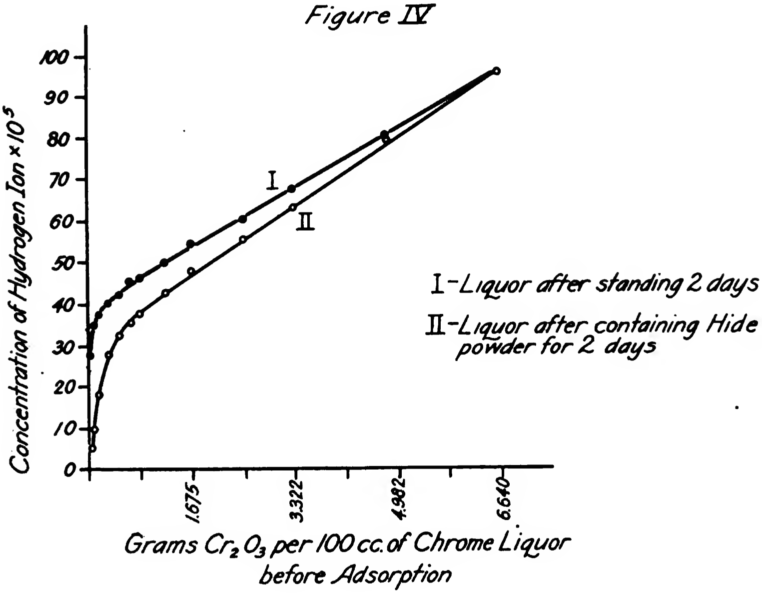
Number of solution	Concentration of hydrogen ion on the chrome liquor: A portion of the liquor after standing 2 days contained gram hydrogen ion per liter	Concentration of hydrogen ion on the chrome liquor: A portion of the liquor after containing hide powder for 2 days contained gram hydrogen ion per liter
1	0.000282	0.000052
2	0.000347	0.000093
3	0.000372	0.000182
4	0.000408	0.000282
5	0.000426	0.000324
6	0.000457	0.000355
7	0.000468	0.000380
8	0.000501	0.000436
9	0.000537	0.000479
10	0.000603	0.000562
11	0.000676	0.000631
12	0.000813	0.000794
13	0.000960	0.000960

DISCUSSION OF RESULTS.

The results on the chromium constituent expressed in the two curves in Fig. 2 are best explained by considering the system to consist of three phases, namely, the chromed-hide substance, an inner solution, and an outer solution. It is probable that the chromium and sulphate, which have been removed from solution, have combined with the collagen constituting the hide substance, to form definite chemical compounds. These compounds vary in composition with the varying concentrations in equilibrium and no doubt more than one is present in a given concentration of the liquor, just as in the case of the basic ferric acetates which are formed with ferric chloride and sodium acetate. This series of

compounds formed from chromium sulphate and collagen constitute the solid phase.

Figure IV



The solid phase may be thought of as a network of a structure similar to that of a foam. The interstices are very small and are filled with what has been referred to as the inner solution. Since these compounds of chromium collagenate are ionizable substances they give up ions to the liquid phase. An electrostatic condition is set up which holds these ions within the sphere of attraction of the large collagen particles which are not free to move since they are in a continuous solid phase. By thermodynamic reasoning it has been shown[3] that under conditions such as these the concentration of the inner solution, that is held within the network of collagen molecules, must be less than that of the outer solution or main body of the liquid.

By the filtration process only one phase, the outer liquid, is separated. There have been two factors at work to change the concentration of Cr_2O_3 in the initial solution, one the formation of the chromium compound, the other the removal of a liquid of

[3] Colloidal Phenomena and the Adsorption Formula, J. A. and W. H. Wilson, *Jour. Am. Chem. Soc.*, 40, 886 (1918).

lesser concentration to form the liquid in the interstices of the collagen network. This second factor has greater influence the more concentrated the chrome liquors which accounts for Curve II (Fig. 2) being lower than Curve I at concentrations greater than that causing maximum adsorption. The colloidal material takes up by imbibition a chrome liquor of lesser concentration and of a lower ratio of sulphate to chromium than that of the main body of the liquid and the amount removed increases with the acidity of the liquor. The increase in hydrogen ion concentration of the liquors with increase in concentration of the constituents is given in Table V and Fig. 4.

The difference in the two curves on the other side of the maximum may also be accounted for. Since the chromed-hide powder before analysis was washed with distilled water, the equilibrium which had existed between the three phases was disturbed, and it may be expected that the action was partially reversed and a portion of the chromium was removed from the hide substance.

The results on the sulphate constituent expressed in the curves in Fig. 3 are explained in a similar manner. The Curve (II) obtained from analysis of the liquor is lower throughout its whole range than the Curve (I) obtained from analysis of the chromed-hide substance. This is because in the case of the sulphate constituent the effect of removing a liquid of lesser concentration to form the liquid in the interstices of the collagen network predominates over that of disturbing the equilibrium by washing the chromed-hide powder.

As is seen from the results in Table V and Fig. 4 the adsorption process causes a decrease in the concentration of hydrogen ion in the liquor. This is largely due to a dilution of the liquor by the removal of the chromium and sulphate constituents. Curve I shows that dilution of the liquid with water reduces somewhat the concentration of hydrogen ion although this is not a direct proportion because the hydrolysis of the basic chromium sulphate acts as a buffer in maintaining the concentration of hydrogen ion more nearly a constant. A comparison of Curve I with Curve II shows that dilution of the liquor by removal of the constituents by the hide powder also reduces the actual acidity. The change in acidity is much greater in the more dilute liquors,

which is to be expected since the amount of the constituents removed is a much greater fraction of the total originally present. At most the acidity is very low since the most acid solution has a lower hydrogen ion concentration than is given by 0.005 M HCl.

In a recent publication Wilson[4] has given 750 as the molecular weight or as a multiple of the equivalent weight of collagen. Using this value he calculated the smallest amount of Cr_2O_3 required to react in equivalent proportions with collagen. This value is 3.38 grams Cr_2O_3 per 100 grams hide substance. The maximum amount of Cr_2O_3 found to combine with hide substance in these experiments is 13.4 grams which is approximately four times the 3.38 given by Wilson. It therefore, follows that 187 may be written as the combining weight of collagen. Or we may speak, at least tentatively, of this substance as a tetrachrome leather. Whether or not a leather can be produced containing a greater amount of fixed chromium has not yet been determined, but it seems that the maximum amount of chromium oxide taken up from a given liquor is 3.38 or some multiple of it and 13.4 is the highest amount so far known.

We are greatly indebted to A. F. Gallun & Sons Co., of Milwaukee, for their generous support of this research and to Mr. John Arthur Wilson for his valuable suggestions.

LABORATORY OF COLLOID CHEMISTRY,
Havemeyer Hall, Columbia University,
New York, N. Y., June, 1919.

TOTAL, SOLUBLE, AND INSOLUBLE ASH IN LEATHER

By J. M. Seltzer.

ADDITION TO THE 1919 COMMITTEE REPORT WITH DISCUSSION OF THE REPORT AT THE ATLANTIC CITY MEETING, MAY 23, 1919.

After submitting our Committee Report to the Editor for publication the Chairman sent the following inquiry to all collaborators:

We wish to inquire whether the ash determinations were run in platinum dishes, also whether a muffle furnace was used or

[4] Theories of Leather Chemistry, J. A. Wilson, this JOURNAL 12, 108 (1917).

whether ignition was made with a burner, if so, the kind of burner used. There is considerable variation in the amount of ash found by ashing the water soluble solution and the extracted leather. In some cases the percentage of total ash found by that method is lower than that found by the direct determinations of the total ash. In most cases, however, the direct determination is very much lower than that found by using the water extracted leather and solutions.

The following replies were received:

J. B. CHURCHILL: Replying to your question regarding the ash determinations I would say that they were all run in platinum dishes of about 150 cc. capacity. They were not ignited in the muffle, but after a preliminary burning over a low flame, were finished by igniting over a No. 4 Meker burner, so adjusted that the dish was brought to a dull red. We tried, so far as possible, to keep the conditions the same.

Regarding the differences which you mention, may I say that I believe that decomposition of the magnesium sulphate can account for a considerable part. It is possible for this to lose sulphuric acid by direct heating and it is also possible to get a considerable reduction when a loaded leather is ignited. In the cases where the direct determination of the ash is much lower than that found from the water extracted leather and solutions, I am wondering whether distilled water was used for extraction. In this laboratory the use of tap water in place of distilled water would have given a figure nearly ½ per cent. higher than would be correct for the soluble ash. I imagine that all laboratories used distilled water for this purpose.

I cannot understand why the results for total ash found by the addition of insoluble and soluble ash should be so much higher than when the total ash is determined directly. I have told you in a previous letter that we are carrying out a rather careful investigation of the effects of igniting magnesium sulphate both alone and in the presence of leather and when this work is completed, it will probably throw considerable light on the variation in the total ash when determined directly. This determination, however, should not vary a great deal when carried out by different laboratories.

I have before me, the total ash determinations on twenty leathers and give them in detail. The determinations in the left hand column were made by this laboratory, those in the right hand column by the Bureau of Standards. They were made independently and several weeks apart; Mr. Young who made the determinations, having no knowledge of the results obtained by the Bureau until reporting to me. It seems to me practically impossible to account for any such variation as you mention in your letter by attributing it to different degrees of ignition. I am repeating the entire work, with three different leathers and will send you the results obtained by the latter part of the week. It seems to me that two sources of error are possible, that may account for the high per cent. of total ash as found by adding 5 + 6. First, that the water used, contains a weighable amount of residue; secondly, that in evaporating the 500 cc. of extract, a certain amount of material was dissolved from the glass. This may seem at first sight somewhat exaggerated; but in other work, I have oftentimes seen glassware that would have yielded enough water soluble material to more than account for this error. In your work I used Jena glass beakers for evaporation and took the precaution to boil these out with distilled water a number of times before using.

CALCULATED FOR 12 PER CENT. MOISTURE.

TOTAL ASH.

Sample	J. B. Churchill C.	Bureau of Standards W.
1	1.18	1.21
2	1.24	1.29
3	1.14	1.14
4	1.35	1.36
5	1.59	1.66
11	0.92	0.99
12	0.86	0.94
13	0.84	0.87
14	0.91	0.88
15	1.14	1.15
21	1.00	0.95
22	0.87	0.88
23	0.86	0.88
24	0.91	0.90
25	1.21	1.17
31	1.06	1.08
32	0.94	0.94
33	0.98	0.96
34	1.01	1.02
35	1.35	1.32

I have just completed the analysis of two leathers for total, insoluble and soluble ash. The two leathers in question were two samples of heavily loaded hemlock sole leather and vary but little in their ash content and water soluble. Sample No. 1 contains about 12 per cent. glucose while No. 2 about 6 per cent. We ran these in accordance with your Committee directions; but in this case, all determinations were made in porcelain. The values for total ash are almost identical in both cases with those previously found when ignitions were made in platinum. My thought in submitting these results to you was simply that they might furnish you with additional information relative to the point you wrote me about.

I think that they indicate that the total of the soluble and insoluble ash as determined by Method No. 5 and No. 6 of your Committee, instructions should be approximately equal to the value for total ash found by Method No. 2.

	Sample 1			Sample 2		
	I.	II.	Av.	Av.	II.	I.
Moisture...	10.25	10.17	10.21	10.27	10.25	10.29
Water sol..	35.91	35.44	35.67	35.50	35.45	35.55
Total ash...	3.09	3.16	3.13	3.20	3.18	3.22
Insol. ash..	0.34	0.32	0.33	0.23	0.24	0.21
Soluble ash.	2.76	2.78	2.77	3.01	3.00	3.02
Total insol. & sol. ash	3.10	3.10	3.10	3.24	3.24	3.23

W. K. ALSOP: The ash determinations were all made in platinum over a Bunsen burner with a gauze top. Some of the results obtained by members of the Committee are difficult to understand.

V. J. MLEJNEK: All the work of ashing was done in platinum dishes in the open air, using an ordinary Bunsen burner, known as the Tyrell or Tirrill burner.

J. S. ROGERS: Total ash made in porcelain, started over Bunsen burner finished in electric muffler. Insoluble ash from above made in platinum, ignited over Meker burner. Ash on the leather residue from the water extraction made in porcelain, started in muffle and finished over Meker burner. Ash on water soluble portion made in rhotanium dishes over Meker burners. Insoluble ash from above made in platinum crucible over Meker burner.

The difference which you mention in the results obtained by different collaborators may be due to different degrees of decomposition of salts present in the leather, for example, Epsom salts may be reduced to magnesium carbonate or oxide by strong ignition in the presence of organic matter.

R. E. PORTER: The ash determinations were made with a Meker burner in a low, wide silica dish. These determinations could have been made in a platinum dish and in muffle furnace but since no specifications were mentioned I did them in the usual manner.

HARRY GORDON, F. F. MARSHALL, S. T. LOWRY: Platinum dishes were used and ignitions made with a Tirrill burner. In ashing "Leather A" by Method No. 2 and analyzing for Epsom salts and sulphates the following results were obtained:

MgO = 0.61 per cent. =C= 3.75 per cent. $MgSO_4.7H_2O$.
SO_3 = 0.26 per cent.

Then determinations of the above materials were made in the soluble portion of the soluble ash (Method No. 6) with the following results:

MgO = 0.25 per cent. =C= 1.50 per cent. $MgSO_4.7H_2O$.
SO_3 = 0.83 per cent.

The insoluble portions of the soluble ash (Method No. 7) were also analyzed for Epsom salts and sulphates with the following results:

MgO = 0.34 per cent. =C= 2.06 per cent. $MgSO_4.7H_2O$.
SO_3 = 0.04 per cent.

Adding up the corresponding parts of the analyses I obtained by Methods No. 6 and No. 7 3.56 per cent. $MgSO_4$ $7H_2O$; 0.59 per cent. MgO and 0.87 per cent. SO_3 as against 3.72 per cent. $MgSO_4$ $7H_2O$ and 0.61 per cent. MgO, 0.26 per cent. SO_3 by Method No. 2.

In observing the percentages of SO_3 obtained by ashing the original leather (Method No. 2) and by ashing the residue of the water soluble material (both soluble and insoluble portion of the soluble ash. Methods No. 6 and No. 7) a difference of 0.61 per cent, SO_3 is noticed, due to the fact that a much larger percentage of the sulphates is reduced in the presence of a larger amount of

carbon when using Method No. 2 than when using Methods No. 6 and No. 7.

I then made a water soluble determination using the Procter extractor and proceeded as under Methods No. 6 and No. 7 with the following results:

ORIGINAL BASIS.

Soluble ash (No. 6) .... 1.77 per cent.
Insol. portion of the sol ash (Method No. 7) 0.50 per cent.

Adding to the insoluble portion of the soluble ash 0.50 per cent., the percentage of copper determined which was 0.14 per cent. about the same result is obtained as when using the Oberfell leather extractor. The results obtained by the Procter method show that sources other than that due to the kind of extractor used account for the high insoluble portion of the soluble ash by Method No. 7 as against Method No. 5.

DISCUSSION.

J. B. CHURCHILL: There isn't much left to say on this subject, except that my recommendation would be that in determining the total ash we keep as near to the same method of burning as is possible and for the insoluble ash, that this be determined from a portion of leather that has been extracted rather than from the extracted solution. I think the difference in the results reported by the members of the Committee comes from the variation in the reduction of magnesium sulphate which is present in the water soluble solution. I do not think there is very much more to add.

J. A. WILSON: Mr. President, for the particular sample that was sent out, there seems very little question that the more nearly true value for total ash was that obtained by adding the ash from the soluble portion to that from the insoluble portion, because there was less reduction. But we would hardly want to use that method of getting the total ash for chrome leathers, because very often you will get a much lower ash by adding those two figures than if you did the ashing directly which seems to be due to the extraction of sulphuric acid in determining the water solubles; there being less sulphuric acid in the insoluble portion, you get a greater reduction of the insoluble sulphates which would remain in the final ash.

Now, there are other types of leathers, such as those loaded with barium sulphate, in which conditions are just the reverse of those with magnesium sulphate, for a compound originally insoluble is rendered soluble by reduction. So we will undoubtedly have to do work with a number of other types of leathers before we can decide on any fixed methods.

J. B. CHURCHILL: In the sugar industry the determination of the ash is of very great importance and there are a variety of methods of doing this, according to what is wished to be shown by the ash determination. For example: one method is to burn the sugar or syrup until thoroughly carbonized, dissolve, filter and wash the carbon, ignite in a platinum dish, add the original filtrate, evaporate to dryness, and ignite. This ash, after being weighed, is moistened with water, exposed to carbon dioxide and dried at a low temperature under vacuum. It is then re-weighed. Another method is to treat the ash as originally found with sulphuric acid and weigh as sulphates. It seems to me that we must take into consideration what we wish to find when we determine the ash in leather. There is probably no one way of determining ash, which will give the correct figure for the mineral constituent of the leather as they originally existed and we can simply accept the figure for ash as giving the amount of carbon free residue left on burning under a specific condition. If, for instance, we wish to find out how much magnesium sulphate the leather originally contained, we would have to make a direct determination of the magnesium present, and we would have to do likewise with other things.

F. P. VEITCH: Mr. Chairman, I think perhaps Mr. Churchill is right—it is a question of what you want the term "ash" to mean. It is an old problem, of course, and one of the systems, as Mr. Churchill says, is to carbonate with carbon dioxide or ammonium carbonate, another is to convert to sulphates.

In this case, you have possibilities like this: Reduction to the oxides in one case, and in others partly to oxides and partly to carbonates. If you want the ash to equal total salts present in the leather, you certainly ought to use an entirely different procedure. If the minimum residue that can be gotten at high temperatures in burning, you have, as I see it, three possibilities:

ignition to oxides, or carbonates, or conversion to sulphates. As I look upon the term "ash," it really ought to mean the minimum residue, that is, the oxides or other compounds stable at the high heat usually employed. Insoluble ash should be determined, I think, as Mr. Seltzer has recommended, by burning the extracted leather.

J. A. Wilson: The only objection to reducing the ash to the oxides lies in the determination of fixed tannins, which we get by difference. The negative radicals then would add themselves on as fixed tannins.

THE APPLICATION OF COLLOID CHEMISTRY TO THE LEATHER INDUSTRY.*

By John Arthur Wilson,
With Discussion by I. D. Garard and Others.

We might have shortened our title without in the least changing its meaning, since any chemistry by application to the manufacture of leather becomes colloid chemistry. The term colloid is added, not as signifying any mysterious variety of chemistry, but rather to denote the application of the chemistry with which we are all familiar to those special conditions existing in the immediate vicinity of surfaces. It is customary to refer to a substance as being in the colloid state when the area of its surfaces per unit weight, known as the specific surface, is very large, say between the arbitrary limits of 50 and 5,000 square meters per gram. All of us, whether tanners or chemists, who are experimenting with processes for making leather are dealing with colloid chemistry, even though the fact may not be recognized, and any broad generalizations which we learn from a study of the subject should serve as guides and short cuts in perfecting our manufacturing processes.

The rapid advance of colloid chemistry at the present time when our ideas concerning atoms and the forces acting between them have been undergoing change has resulted in some confusion in the literature through the earlier acceptance of the newer views by some writers than by others; and this is partly

* Read at the Annual Meeting of the A. L. C. A. at Atlantic City, May 22, 1919.

responsible for the difficulties experienced by persons beginning an independent study of the subject. Every leather chemist is necessarily a colloid chemist and may be presumed to be familiar at least with the elementary principles of the subject such as are to be found in the five or six books on colloid chemistry which have appeared during the past few years. It does seem desirable, however, before discussing practical applications, to mention briefly certain ideas having an important bearing upon our problems, but which have been advanced so recently that they have not yet found their way into these text books.

A radical change in our conception of the nature of solid matter has resulted from the work of W. H. and W. L. Bragg[1] on the structure of crystals. By using the idea originated by Laue that a crystal constitutes an effective diffraction grating for X-rays, they have developed a method for determining the exact arrangement of atoms in a crystal. The examination of many types of crystals has established the fact that crystals in general are not built up of molecules, as we formerly supposed, but simply of atoms arranged in definite patterns. In a sodium-chloride crystal, the sodium and chlorine atoms alternate along three sets of lines at right angles to each other, forming a simple cubic lattice, each sodium atom being surrounded by 6 equidistant chlorine atoms and each chlorine atom by 6 equidistant sodium atoms. In the diamond, each carbon atom is surrounded by four others equidistant from it, just as the four corners of a regular tetrahedron are arranged around its center of gravity.

This work forms the starting point for an extensive theory of the constitution of solids and liquids developed by Langmuir,[2] who reasons that in the sodium chloride crystal each sodium atom must share its valence with 6 chlorine atoms and each chlorine atom its valence with 6 sodium atoms, and that this general sharing of valence continues throughout the entire crystal, from which it follows that the cohesive forces holding the crystal together are chemical, since they operate directly between the atoms. If a molecule be defined as a group of atoms held together by chemical forces, then a crystal, or according to Langmuir any solid body, may be looked upon as a single large

[1] X-Rays and Crystal Structure (The MacMillan Co., New York).
[2] *Am. Chem. Soc.*, 38, 2221 (1916) and 39, 1848 (1917).

molecule. But when a salt crystal is heated, the sodium and chlorine atoms leave the surface in pairs, forming simple molecules of only 2 atoms each; it is, therefore, proper to consider evaporation and condensation as chemical processes. Equally startling conclusions may be drawn from other applications of these recent discoveries, but we are concerned particularly with the information they give us of conditions obtaining at the surfaces of bodies.

Let us consider for a moment the diamond whose structure emphasizes very strongly the tetravalent character of carbon. Any atom within the interior of the crystal will have all of its primary valence saturated, but an atom at the surface must have at least one valence directed away from the crystal and, therefore, unsaturated, leaving it available to combine chemically with other atoms. Langmuir has shown that the surface atoms of a carbon filament actually do combine with 1 atom each of oxygen when the filament is heated in an atmosphere of this gas, which indicates that half of the valence of the surface carbon atoms is available for chemical combination. I believe that the existence of this free primary valence at the surfaces is responsible for the great adsorptive power of finely divided carbon.

When atoms combine by means of primary valence, there is always left a certain amount of residual or scattered valence. The compounds K_2O and SO_3 furnish examples of atoms held together by primary valence, but these two groups of atoms still possess sufficient residual valence to unite them to form the fairly stable substance K_2SO_4. This secondary form of valence results from incomplete saturation of primary valence and where conditions are such as to prevent the combination of atoms by primary valence, this latter may be turned completely into secondary or scattered valence. For example, in gaseous sodium chloride the 2 atoms in each molecule are held together by primary valence, but in a salt crystal, since we can hardly consider sodium as hexavalent, we must conclude that the primary valence has been scattered and that the atoms are held together entirely by secondary valence. There will always be some free valence associated with the atoms at the surface of a body, although it may be either of the primary or secondary type. As Langmuir puts it, in the case of a crystal, the surface must be looked upon

as a sort of checker-board containing a definite number of atoms of definite kinds arranged in plane lattice formation, the spaces between and immediately above these atoms being surrounded by a field of electromagnetic force more intense than that between the atoms inside the crystal.

A direct result of the free valence upon the surface of bodies is the tendency for the surface atoms to combine chemically with molecules, atoms, and ions striking them. Such combination is generally reversible, just as most of the simpler types of chemical reactions are reversible, and likewise it is selective, but its extent is largely dependent upon the specific surface of the body. I feel convinced that those phenomena which we class under the title *adsorption* are generally the result of chemical combinations such as we have just described.

In every sol the colloid particles are electrically charged, which may be due either to the giving off of ions by the surface of the particles or to the adsorption from the solution of ions of one sign to a greater extent than those of the other. This electrical charge is apparently necessary to the stability of the sol and probably operates by preventing coalescence; the particles being charged alike repel each other. Associated with the electrical charge on any particle will be an equivalent number of ions of opposite sign, which, although actually in solution, cannot diffuse more than a short distance from the surface of the particle because of the existing electrochemical attractions; in other words, these ions are confined to a thin film of solution surrounding the particle. Other ions from the solution proper may freely diffuse into and out from this film, but the presence of ions balanced only by the charge on the particle will result in a distribution of ions in this surface film different from that in the rest of the solution, which in turn will cause to be set up between these two phases an electrical difference of potential of very great importance to the leather chemist, as I shall attempt to show presently.

Langmuir's theory of the atomic structure of solids adds weight to the theory advanced by Procter long ago regarding the structure of gelatin and hide substance. Procter looks upon gelatin as a molecular network with interstices of molecular dimensions, complicated chains of amino acids being peculiarly

fitted to produce such a structure. According to his view, a plate of gelatin or a hide fiber consists of a single large molecule built up of a network of atoms, the simpler molecules existing in a gelatin solution having lost their identities upon setting.

When a gelatine plate, or a hide, is immersed in a solution of an acid, say of HCl, the solution readily diffuses into the interstices and some of the hydrogen ions striking the network become chemically combined, probably with certain of the nitrogen atoms, giving the network a positive electrical charge, and the corresponding chloride ions are prevented from leaving the absorbed solution by the electrochemical attractions of the charges on the network. On the other hand, water and positive and negative ions in equivalent numbers may readily diffuse into or out from this absorbed solution; but at equilibrium, because of the presence of the chloride ions associated with the charge on the gelatin network, the absorbed solution will have a distribution of ions different from that in the surrounding solution and consequently there will be set up an electrical difference of potential between these two phases, just as in the case of a sol there is a potential difference between the surface film of solution surrounding a particle and the bulk of solution. The difference between a sol and gel appears to be largely one of continuity; the gelatin in a sol is discontinuous, but when the particles touch in such a way as to form a continuous network, the system sets to a gel.

Another important subject is that of the swelling of gelatin or hide in aqueous solutions, but this has been treated so frequently in our JOURNAL that it seems only necessary in passing to mention that the distribution of ions between the solution absorbed by the gelatin and the remaining external solution operates so that the absorbed solution will always have a greater concentration of ions than the external solution and this gives rise to pressures causing the gelatin to swell until the cohesive forces of the gelatin balance the excess diffusion pressure of the ions of the jelly phase. The degree of swelling is directly proportional to the excess of concentration of diffusible ions of the jelly and may be varied at will between certain limits by altering the concentrations of electrolytes in the solution. Many of the theoretical conclusions of this work were derived mathematically and are, there-

fore, hardly suitable for discussion in a talk of this kind, but should be studied in the original papers.[3]

The fact that the available literature contains mention of only very few practical applications of these principles is in itself no proof that the principles have not been extensively applied, but anyone who had profited by certain theories would in all probability encourage their further development, and since active interest in this work has been so narrowly confined, I feel that there has been a general lack of appreciation of its practical value. The work as it stands contains several quantitative formulas which, in the hands of a chemist skilled in making leather, should serve as invaluable guides wherever it is found necessary to alter manufacturing conditions or to locate the causes of occasional difficulties; but there still remains a great deal to be done before we can expect the work to produce the desired uplifting effect upon the industry as a whole. There seems little use in appealing for greater co-operation until sufficient interest has been aroused in the work itself, and it is in the hope of arousing such interest that I shall resort to a little speculation in discussing the application of theory to one or two general processes.

Not least in complexity of the operations involved in making leather is that of vegetable tanning. The numerous tanning materials available vary widely in astringency and diffusibility and modify each others actions when used in mixtures. The behavior of a tan liquor depends, not only upon the kinds and amounts of tanning materials used, but also very largely upon the amounts of non-tannin matters present, such as lime, acids, and salts. When a tanner is called upon to produce a leather with some

[3] The Equilibrium of Dilute Hydrochloric Acid and Gelatine, *Jour. Chem. Soc.* 105, 313 (1914): This JOURNAL 9, 207 (1914).

The Acid-Gelatin Equilibrium, *Jour. Chem. Soc.* 109, 307 (1916); This JOURNAL 11, 261 (1916).

The Swelling of Colloid Jellies, This JOURNAL 11, 399 (1916).

Theory of Colloids, *Jour. Am. Chem. Soc.* 38, 1982 (1916); This JOURNAL 12, 122 (1917).

Theory of Vegetable Tanning, *Jour. Chem. Soc.* 109, 1327 (1916); This JOURNAL 12, 76 (1917).

Theory of Tanning, This JOURNAL 13, 177 (1918).

Colloidal Phenomena and the Adsorption Formula, *Jour. Am. Chem. Soc.* 40, 886 (1918).

new properties, he is confronted by an almost infinite number of possibilities in the matter of preparing his tan liquors, so that if he worked solely by chance, there would be little or no hope of his ever mixing just the right materials under the right conditions to make a liquor capable of producing the desired properties to the highest degree. If we, as leather chemists, are not striving to bring our science to such a state as to enable one to calculate how to proceed in such a case, we are failing in what is perhaps the chief duty of our calling.

No one, so far as I know, has discovered just why certain tanning materials are very astringent and others mild in action. Any reasonable explanation is better than none, so I have ventured the guess that the astringency of a tanning material is a function of the magnitude of the electrical charge on the particles, the greater the charge the greater the astringency. Had not Professor Thomas been called to France, he would probably by now have subjected this idea to the rigid test of experiment. Although he is scheduled to return in the very near future, it will probably take several months at least to get the desired experimental data. Meanwhile it is interesting to note what bearing it will have upon the science and practice of tanning, if the guess ultimately proves to be correct.

The experimental fact which we do possess at the moment is that tannin particles are all negatively charged in aqueous solutions. Therefore, in the surface film of solution surrounding each particle there will be a number of positive ions associated with and equivalent to the electrical charge on the particle, the presence of which will cause a distribution of ions in the surface film different from that in the bulk of solution, which in turn will cause a difference of potential to be set up between these two phases. In practice tan liquors are always slightly acid and through chemical combination with hydrogen ions the collagen network will assume a positive electrical charge and an electrical potential difference will be set up between the solution absorbed by the hide substance and the tan liquor, but of opposite sign to that set up between the surface film surrounding a tannin particle and the tan liquor. It is my opinion that the astringency of a tanning material in practice is largely determined by the sum of

these two potential differences, the variation of which will produce widely different results.

Consider the case where the absolute value of each potential difference is a maximum. The tannins would be very astringent and combine so vigorously with the hide as to prevent their penetrating very far. But these conditions also favor great swelling of the hide and we should have antagonistic actions, since the tannins would tend to contract the swelling hide substance. A very pretty example of such a condition is to be found in a paper by Sheppard and Elliott,[4] who have shown that if a photographic negative be treated with a mixture of acetic and tannic acids, the gelatin layer becomes wrinkled or corrugated, the network of puckers forming a pattern, apparently due to alternate hardening and softening effects, the ridges being more swollen and the valleys more tanned. It is not uncommon when experimenting with new combinations to have the skins come out of the liquor looking as though they had been embossed.

Suppose now that the absolute values of the two potential differences under consideration were made as small as possible. A certain potential difference is required to keep the tannin particles from coalescing, and with some materials, if not with all, we should get precipitation of the tannins. The hide would contract, but there would be little or no tanning action.

Between these two extremes we should get a great variety of possibilities; the astringency of the tannins should fall from a maximum to a minimum and the rate of penetration of the tannins into the hide fibers and the degree of plumping should vary, and each of these variable factors would in turn have an effect upon the properties of the finished leather.

With sufficient experimental data and an application of higher mathematics, it should be possible to derive an equation comprehensive enough to enable us simply to calculate how to proceed to make leather possessing any desired properties to a maximum extent. This is no wild dream for we have already made a considerable start in this direction by deriving equations for the potential differences between the tan liquor and the surface film surrounding the tannin particles on the one hand and between the liquor and the solution absorbed by the hide fibers on the

[4] The Reticulation of Gelatine, *J. I. E. C.* 10, 727 (1918).

other. The potential difference is given as a function of both the concentration of ionized electrolyte in the liquor, called x, and the concentration of ions associated with the electrical charge on the colloid, called z,

$$E = \frac{RT}{F} \quad \text{Log} \frac{2x}{-z + \sqrt{4x^2 + z^2}}.$$

Other conditions being the same, the value for z will probably always be higher for an astringent tannin than for a milder one. With x nearly constant, any increase in z raises the potential difference; while it is lowered if x is increased while z remains nearly constant. In general, increasing the concentration of common salt will lower both potential differences and in some cases will actually cause a precipitation of tannins. With the start we have got, there is reason to hope that we shall soon have the process of vegetable tanning upon a really scientific basis.

The process of fat liquoring has many points in common with that of tanning only here we bring about the electrical charging of the oil globules ourselves, during the preparation of the emulsion; for example, by shaking up an oil with soap, we cause the negative ions of the soap to be adsorbed at the surfaces of the oil globules, giving each globule a negative electrical charge which then prevents them from coalescing. In the case of an emulsion of cylinder oil, Powis[5] has shown that so long as the potential difference between the solution and the surface film surrounding each globule has an absolute value greater than 0.03 volt, the emulsion is stable; otherwise it is soon broken up.

Before closing I wish to call your attention to the task recently undertaken by the British Association for the Advancement of Science of compiling each year a report on Colloid Chemistry and its Industrial Applications. Two volumes have already appeared and you will find Professor Procter's contribution "Colloid Chemistry of Tanning," which is reprinted in the May JOURNAL, well worth reading.

Lewis [6] says that one of the chief reasons why colloid chemistry has not found wider industrial application is that the pure science has not been advanced sufficiently. In the leather industry, however, due to Procter's extensive researches the science

[5] *Z. physik. Chem.* 89, 186 (1914).

[6] *J. S. C. I.* 38, 1 (1919).

has far outstripped its applications and there is much available in the pure science that could be turned into profit, if it were only better appreciated. Procter has laid a good foundation, but it needs further development, and the industry could well afford to support the research necessary to bring this work to the point where it will be of material assistance to tanners knowing nothing of chemistry as a science.

Discussion.

Dr. I. D. Garard: There is no adverse comment that I wish to offer regarding Mr. Wilson's paper. I might say in discussing the subject of colloids that it is a pure science, and a great difficulty confronts the student in the fact that there is considerable confusion of terms in the literature, or rather, perhaps duplication of terms. We have numerous classifications of colloids that confuse one who is just beginning to study the subject. This is perhaps more or less unjustifiable, but since the workers have worked in different places, and since the science is a new one, it is more or less inevitable that there should be this confusion.

We ought to be able to predict in any kind of chemistry just what is going to happen under a given set of conditions. If we have a reaction between sulphuric acid and alcohol, we know that by varying the conditions, we can produce ether or ethylene, whichever we choose, almost to the exclusion of the other.

Now, we cannot do that in the chemistry of colloids, largely because of the fact that we are not sufficiently familiar with the laws involved; they haven't been studied for a sufficient length of time. There are certain principles that have been studied, of course, but there are many things that are not very well understood.

In commenting on Langmuir's paper, which Mr. Wilson spoke of several times, his idea so far as it applies to solids is quite good. However, if you have read his paper, and no doubt many of you have, you will find that he also applies it to liquids. I think he is going a little too far here. He says that the evaporation of a liquid is a chemical change. It may be, but the evidence does not seem convincing. However, his work is undoubtedly an advance in chemical theory.

Now, Langmuir is advancing a hypothesis. Mr. Wilson has advanced a hypothesis in the process of tanning. If we are going to make any real progress in science, it is necessary, to my mind, for the hypothesis to precede experimentation. Most anybody can go to the laboratory and perform experiments, but unless he has something in mind, he will probably not succeed in proving anything.

There are a number of industries which have profited greatly from the application of colloidal principles, not always in the same way, of course, because there are a number of principles in this branch of chemistry. We might mention a few of them, some of which are familiar.

Photography has benefited by the science a great deal. And there is the manufacture of mirrors, for instance. The manufacture of silver mirrors depends upon the reduction of silver salts to metallic silver, and its deposition on the glass. That all seems very easy, and it isn't very hard, except that the character of the film deposited depends on the nature of the solution.

There are a number of other industries that I could name, notably the dyeing industry, and the soap industry; soap is one of our most prominent colloids. I was talking a while ago with the inventor of "solid alcohol"—a small industry in itself now—and he told me of the difficulties he had in bringing about that product. But he wasn't familiar with the principles of colloids, so far as they are known. If he had been, a good many of these difficulties, I think, would have vanished.

The production of emulsions might be mentioned. That isn't exactly an industry, except as applied to pharmaceutical preparations, but there are many emulsions that we make and try to keep, and often we find some difficulty in so doing. Then there are some emulsions which we try to avoid, or destroy, because they are injurious in some process that we are going about.

This leads me to say just a word about the classification of colloidal substances, though, of course, no substance is a colloid. In other words, the term colloid or colloidal is used correctly to mean the state in which a substance exists at a given time. The same substance may be colloidal at one time, and have all the properties of a crystalloid under a different set of conditions. Ordinarily we speak of two classes; (*a*) suspensoids, such as the

metals, gold, silver, platinum, etc., dispersed in water or other media, and (*b*) the emulsoids which are represented by gelatin, albumen, starch, and many others mostly organic compounds, and hydroxides of metals. We should expect emulsions to be emulsoids, but they are not always so. If we take a simple case of an emulsion of a hydrocarbon oil and water, most anybody would say that it is an emulsoid; it shows the Brownian movement, the particles of oil can be precipitated with salt, and they can be separated by ultrafiltration. So that while this is a case of the dispersion of one liquid in another, it seems to hold pretty closely to the laws which are known to apply to suspensoids.

Colloidal particles in general carry electrical charges; I guess they all do, that seems to be pretty well proved by now. Suspensoids are very definite in this property; they are either positive or negative. On the other hand, some emulsoids seem to have no charge in neutral dispersion media, but the character of their electric charge depends upon the character of the liquid in which it is dispersed. Take for example gelatin; if gelatin is in a slightly acid solution, it is a positive colloid; in an alkaline solution, it is a negative colloid. How to determine the charge on a sol is a question that confuses some. The most obvious way is to put the colloidal dispersion in an electrical field, and see which way it migrates.

It was thought at one time, and you will find it given in one of the current books on this subject, that if you hang strips of filter paper in a dispersion, the charge may be determined. Under these conditions, the negative sols were supposed to ascend the strips of paper and the positive sols to coagulate at the point of contact of the paper and the sol. The theory was that the paper is charged positively with respect to water, and so attracted the negative sol, but repulsed the positive.

That is in one of the modern books but it has been disproved, and the phenomenon is probably merely a matter of concentration, and not electric charge at all. If any sol is concentrated, it will coagulate and if dilute, it will ascend the paper. Another method sometimes used to determine the charge is coprecipitation. In this method, a sol of known charge is added to the unknown. If coagulation occurs, the unknown is charged oppositely to the known. If it doesn't coagulate, we are not quite sure what it is,

because there is a definite relative concentration necessary to produce coagulation, with which fact you are probably familiar. If you exceed that concentration, or don't quite reach it, one sol only serves to protect the other, and the precipitation, or rather the coagulation of the mixture is more difficult than that of either sol alone.

A very simple reaction illustrates some properties of colloids, and that is the purification of casein. It sounds very simple, but it isn't quite as simple as it sounds. If you make a dispersion of casein, with dilute alkali, it looks very much like milk. Now, if you add acid to precipitate it, it depends on how much you add whether it comes down, because casein may take a positive charge in the acid, and you will have an acid dispersion, just as you had an alkaline dispersion.

One of the features that perhaps concerns the leather industry more than any other of the pure science experiments is the swelling of gelatin. Procter's work on gelatin has shown a great many things concerning the swelling. A great many things have been established, but a great many more remain to be established. Just what the effect of various salts is, is not known. It is found that certain salts produce much less swelling than others. I believe of those that have been tried, potassium citrate has the least effect. There has been a good deal of work done on this problem, but unfortunately, the work was not very complete and so it is hard to interpret.

There are a number of other substances that the tanner deals with, such as vegetable tannins, mineral tannins, dyes—they are all colloidal dispersions. It seems possible that with experimentations on gelatin in a number of cases we may find out something of very considerable importance with reference to hides, which are very similar to gelatin in chemical composition.

Lastly, I want to mention one more point, and that is in regard to enzymes. Perhaps we think the study of that is organic chemistry, but it is more nearly colloidal chemistry. If you prepare an enzyme in a reasonable state of purity, you deal entirely with the principles of colloidal chemistry; organic chemistry enters into it scarcely at all. The technique of working with enzymes is very difficult, since it requires very accurate control. You will find in the literature, statements of the optimum activity of

pancreatin, for instance, which are wrong; the reason for that is this: The optimum acidity for the amylolytic activity is almost neutral, with the presence of an electrolyte of some sort. But the reason for the misleading statements is because the most nearly pure water you can make by distillation from alkali has a hydrogen ion concentration of something like 5.6 (Sorensen Scale), so that the water is slightly acid. Now, the optimum for pancreatin is between that and theoretical neutral (7.0). Consequently, to the best water you can get, you must add a little alkali to get the best reaction.

The activity and deterioration of enzymes are susceptible to a number of things. They are protected by many things in solution. If you have the substrate present, that is the material upon which the enzyme is acting, the enzyme doesn't deteriorate nearly as rapidly as it does without it. In alcoholic solutions, the deterioration isn't as great as in water.

There are a multitude of things that enter into the action and the purification of enzymes, which need to be explained very much more fully than they have been, and I am not just sure how familiar the leather chemists are with the technique of enzymes; perhaps they are quite familiar with it, but in case they are not, there certainly must be very considerable room for improvement of processes by a close control of enzymatic action, as well as of the various other tanning processes.

A. A. CLAFLIN: There are certain experiments that we have been undertaking which Mr. Wilson's paper will probably shed considerable light on. The original work done was on the influence of acids on the viscosity of the gluten of wheat. Last year when they were conserving the wheat of the country, they tried to replace wheat with a number of different flours, and they found they got into trouble because the glutens and the proteids of the various grains didn't have the same viscosity that the gluten of the wheat had, and we found that very small amounts of acid increased the viscosity to some extent in all the natural glutens, and more so in the gluten of the wheat than in the glutens of the other grains.

We are working on a continuation of the same line; we have been experimenting and finding out the effect of the nature and of the size of the media on the viscosity of the solutions, and also

on the stiffness of the gels, to see whether it was simply a function of the organic concentration, or of the nature of the acids or alkalis used. The experiments haven't been carried far enough forward yet to say anything about them. Dr. Costin is the man who is doing the work, but it seems as if there was a certain relation between the viscosity of the gelatins and albumens in solution and the stiffness of the jellies, and it would seem as if they were related to the concentration of the acid. I would like to ask Mr. Wilson how much he can predict on that line of work?

J. A. WILSON: Mr. Claflin's remarks serve to emphasize the wide application of these principles which might seem to be the exclusive property of the leather chemist. The work he mentions requires a knowledge of the very same basic laws that are involved in really scientific control of pickling, or of chrome or vegetable tanning. In my work I have done very little experimenting with changes in viscosity, but the data available indicates that viscosity of gelatin and other protein solutions is a function of the concentration of electrolytes present very similar to that of the degree of swelling for which we have already derived quantitative relations. I have found these equations very useful in predicting practical results and see no reason why they could not be applied to Mr. Claflin's problems.

J. H. YOCUM: Might I ask Mr. Wilson if he could describe in any quantitative manner the plumping effect of the ions and various acids that exist in tanning liquors, so that one could in a measure be able to estimate the effect of these acids as plumping agents? I mean simply as plumping agents—what their concentrations and efficiencies might be.

J. A. WILSON: Vegetable-tan liquors are extremely complicated systems about which we still have much to learn, but we hope, by a continuation of our work on colloids, to derive quantitative relations between plumping, rate of tanning, and speed of penetration on the one hand and the chemical composition of the liquor on the other. At present we can give you a definite relation between plumping and the concentration of acid and salt in pickling, but, in tanning, matters are complicated by the contracting action of the tannins. In pure hydrochloric acid a concentration of about 0.005 normal produces the greatest possible

swelling; if the acidity is either reduced or increased from this point, the hide contracts. The active constituent of the acid is, as you all know, the hydrogen ion, and it is this substance that largely determines the degree of plumping. Weak acids, like acetic, are so little ionized that very strong solutions are required to produce maximum plumping. When added to acid solutions, neutral salts cause a contraction of the swollen hide, but when added to neutral solutions, they cause a slight swelling. However, a hide plumped to a maximum would probably make a very poor leather.

R. H. EAGLES: In speaking of an emulsion of oil in soap solution, Mr. Wilson said that the soap prevented the oil globules from coalescing. Now I understood that the contrary was the case and will cite two instances. One is in the production of crude oil which contains an emulsion of salt water. One method of getting rid of this undesirable emulsion is to add some soap solution. Another instance is in the flotation of minerals, where the presence of traces of soap will destroy the emulsion.

J. A. WILSON: In both of the cases you mention it would appear that the globules or particles possessed positive electrical charges before the addition of soap. The adsorption of a small amount of stearate ions would naturally lessen this positive charge and favor coalescence. But, if an excess of soap were added and the stearate ions further adsorbed, the electrical charge on the globules would become more and more strongly negative and the emulsion would again become stable. In the case which I mentioned, the oil is initially neutral and cannot form a stable emulsion until the particles become charged. The addition of soap furnishes this charge and a stable emulsion results.

L. M. WHITMORE: Take an emulsion of oil in water with a certain amount of alkali, or soap, or acid, if you should add acid or iron salts, the emulsion would be broken up. Whether that is just precipitation of the soap, or not, or whether it is due to the fact of the iron salts being present, I do not know, but if you carry it further than that, the emulsion will go over to the other side, and you will get an emulsion of water in oil. You can start out with an emulsion of 20 per cent. of oil, and the oil will be emulsified in the water, and if an excess of a salt of iron

or chromium is added the system will go over into an emulsion of water in oil.

DR. GARARD: There is no essential difference between an emulsion of oil in water and water in oil. If you take a soap solution of oil, you can get all percentage compositions, I believe, from 1 per cent. soap to 99 per cent. soap, the remainder being oil.

In the case of precipitation with aluminum, chromium, and iron salts, it should be noted, in the case of all emulsions and suspensions as well, that electrolytes have a precipitating effect; it makes no difference what the electrolyte is. Generally speaking, acids have the greatest effect, alkalis greater than neutral salts, and neutral salts the least effect, but there is a precipitating effect in all cases.

MEMBER: Mr. President, I have a distinct contradiction to make to one of the remarks just made, in that, if an oil is combined with 50 per cent. of water solution, an addition of metallic salt will cause no precipitation; on the other hand, it will cause permanent solution which can stand without any precipitation.

R. H. EAGLES: I would like to bring up another point in that respect. In dealing with dissolved proteid in liquors, I have found in precipitating with sulphuric acid that you must bring it to substantial neutrality, whereas only one-twentieth of this amount of acid is required if it contains up to 1 per cent. of chrome salts.

DR. GARARD: One thing I neglected to mention and which applies to the second statement is that, other things being equal, ions of higher valency have greater precipitating effects than those of lower valency, so it is easily conceivable that a salt may precipitate to a greater extent than a monobasic acid. As regards the first statement, so far as I know, there is a minimum amount of metallic salt required for coagulation in a given case. Now, while this emulsion of soap and oil may have been permanent with a metallic salt present, the question is whether or not it would be permanent with more salt. That is a question, of course, that must be considered. There is a minimum point, below which no precipitation will be effected by electrolytes.

JOHN H. YOCUM: It would appear as though a discussion of this type wouldn't be of great moment to the leather chemists

unless it could be shown to be applicable to their industry. As a matter of fact, many of these subjects ought entirely to be fought out and discussed from the points of view of which we average chemists have only a smattering knowledge.

The truth of the matter is that what we want is something that we can use, use in our business, use in our every-day operations. One of those things is the proper determination and estimation of the plumping action of an acid in the presence of its controllers or electrolytes, or what not, in the tanning liquor. What we desire is to know what and where and how we can effect the things that the tanner wants to know. The tanner is quite as anxious as we are to know what the actual plumping value of his acid is, and here we hear "ionization" and measures of ionization that would require the extremes of laboratory experience by the operators, with a lack of accuracy upon their own parts, and machinery and apparatus that would be wholly impossible.

This organization, to my mind, is one that should assist the tanner, and not go into such academic discussions as this.

J. A. Wilson: Mr. President, we are working to fulfil Mr. Yocum's desire to the best of our ability, and I hope that we will get there some of these days; but we have exactly that object in view.

Dr. Thomas Blackadder: I feel that this discussion should not close without a few remarks of appreciation for Mr. Wilson's paper and Dr. Garard's remarks. It seems to me that there are great possibilities in the theory that Mr. Wilson has offered for tanning; he advanced a hypothesis, and that to me is the most hopeful sign, because without a hypothesis, we are sort of at a disadvantage in our research work. But given a hypothesis, we either seek to prove it or disprove it, according to our natural bend, and in that way we will get a further and a truer knowledge of the subject; and therefore, it would seem to me that we should all enter into a discussion of this subject. I hope that Dr. Garard will visit us at our next annual meeting, and that we shall hear a wider discussion among the members of the Association on the subject which has been discussed to-day.

Chairman: I think we all realize that in opening up a new field of research similar to the field which Mr. Wilson and Dr.

Garard are operating in, that it will be necessary to limit the field of operation by the use of more or less ambiguous terms, terms which aren't quite clear in their meaning. But, as we become more familiar with the principles which are established, we can apply those principles and produce very practical results, and I am sure that Mr. Yocum will be the first to concede that work such as Mr. Wilson and Dr. Garard, and other colloidal chemists are doing, is full of hope for the future in its practical application to the leather industry. And I am sure that the majority of us will join in giving those workers the fullest kind of encouragement.

THE DETERMINATION OF FREE SULPHURIC ACID IN LEATHER.

DISCUSSION OF COMMITTEE REPORT AT THE ATLANTIC CITY MEETING MAY 22, 1919.

[Mr. Churchill read his report which was published in full in the June issue.]

CHAIRMAN: Gentlemen, I think you will all agree with me that Mr. Churchill's report is quite the most comprehensive contribution to the solution of this problem of determining the free acid in leather that we have had in some time, and I think Mr. Churchill and his Committee are to be congratulated upon the results of their efforts.

J. S. ROGERS: Mr. Chairman, I think that Mr. Churchill is certainly to be congratulated. I feel that the results of his work show that the Procter and Searle method, with the slight modifications, or improvements that he has suggested, undoubtedly will give us very satisfactory results.

The points brought out, especially with regard to the complete ignition, are without question true, and it is very evident that larger amounts of sodium carbonate are required in the case of loaded leathers.

There is one point that Mr. Churchill did not mention, and I do not know that it is of great importance. In the digestion of the residue with tenth normal acid, it is well known that any iron or aluminum compounds which have been long ignited become difficultly soluble, and it is possible under certain con-

ditions that more of these salts would be dissolved than under other conditions. The solubility of these salts will be affected by the length of time of ignition of the residue.

J. B. CHURCHILL: I would like to say that in case aluminum salts are present they will not affect the determination greatly if the leather is ignited with sufficient sodium carbonate; ignited under these conditions, the residue from such salts will not have an appreciable effect on the determination. If not enough sodium carbonate is added, ignited aluminum oxide may be produced which is insoluble in dilute acids. On the other hand, the residue left from iron salts will not dissolve in the tenth normal acid except to a slight extent. I think, however, that we can eliminate from this discussion the effect of iron salts on the acidity determination as they are not apt to be present in quantity, except on rare occasions.

I think that where more than the normal amount of sulphuric acid is found, for instance, if the determination should show an acidity of 1¾ per cent. of free sulphuric acid present in a sample, it would be extremely desirable in such a case to make as thorough a study as is possible of the cause of this acidity. It would be well to know whether or not such leathers have been treated with sulphite cellulose, etc., and the per cents. and nature of the mineral salts contained. It seems to me most important that we should know the cause of the acidity in such cases before condemning the leather on account of the per cent. of free acid contained.

J. S. ROGERS: I would like to ask Mr. Churchill if he has determined the ash approximately, so that some idea of the amount of sodium carbonate required can be obtained before the sulphuric acid determination is made.

I thought it might be possible from the ash determination alone or from the determination of magnesium sulphate to foretell how much alkali should be used for the determination of acidity. If the ash content or the magnesium sulphate content is known it should be possible to determine whether 25 or 50 cc. of sodium carbonate should be used in determining the acidity.

J. B. CHURCHILL: You might use 35 cc. which would be ample in all cases, making the method uniform.

ABSTRACTS.

Furfural Condensation Products of Tannins and Their Use in Tannin Analysis. By R. LAUFFMANN, *Ledertech. Runds.* 10, 97 (1918); *Chem. Zentr.* 90, II., 299 (1919); *J. S. C. I.* 38, 378A (1919). Like formaldehyde, furfural gives condensation products with tannins on boiling in hydrochloric acid solution, and the reaction may be used for discriminating between and evaluating various kinds of tannin. The procedure is to boil for half an hour, under a reflux condenser, 50 cc. of standard tannin solution with 20 cc. each of 7 per cent. furfural solution and 20 per cent. hydrochloric acid, the brownish or blackish brown precipitate is collected on a tared filter paper, washed, and dried till of constant weight, and calculated to the basis of 100 parts of dry tannin. The "furfural precipitation numbers" thus obtained show close agreement with similar numbers given by formaldehyde precipitation of the same variety of tannin (abstract this JOURNAL 13, 222 (1918). If, to the filtrate obtained above, a few drops of 1 per cent. iron alum solution and solid sodium acetate are added, a bright green zone is formed above the latter by protocatechuic tannins, and a violet zone by pyrogallol tannins which is visible when only a small proportion of the latter is present, so that by means of the reaction pyrogallol tannins may be detected in presence of protocatechuic tannins.

Gravimetric Determination of Phosphoric Acid. By L. W. WINKLER, *Z. angew. Chem.*, 1919, 32, 99; *J. S. C. I.* 38, 391A (1919). A critical examination of the determination of phosphoric acid by precipitation as ammonium magnesium phosphate. The phosphate solution, measuring 100 cc. and containing about 0.1 gram of P_2O_5, is treated with 2.5 grams of ammonium chloride, boiled, 10 cc. of 10 per cent. ammonia is added, followed by 0.5 cc. of magnesium sulphate solution (magnesium sulphate, 10, ammonium chloride, 5 grams, water, to 100 cc.). The hot mixture is stirred until the precipitate becomes crystalline, a further 9.5 cc. of the magnesium sulphate solution is added slowly, and when the mixture is quite cold, the precipitate is collected, washed with 1 per cent. of ammonia, dried, and weighed. The precipitate may be converted into magnesium pyrophosphate by ignition before being weighed. With quantities of magnesium pyrophosphate varying from 0.05 to 0.25 gram, the weight found is about 0.3 milligram too high. Potassium and sodium chlorides do not interfere when the precipitate is weighed as ammonium magnesium phosphate, but the presence of potassium chloride causes the result to be too high if the precipitate is ignited to pyrophosphate before being weighed. The figures obtained are slightly too high when the phosphoric acid has been precipitated previously as ammonium phosphomolybdate in order to separate it from iron, calcium, etc.

Phosphoric Acid; Gravimetric Determination of—as Magnesium Pyrophosphate. By Z. KARAOGLANOW, *Z. anal. Chem.*, 1918, 57, 497-541; *J. S. C. I.* 38, 392A (1919). Investigation of the various methods for the precipitation of ammonium magnesium phosphate showed that the results

obtained are to some extent dependent on the temperature of precipitation, method of precipitation (slow or rapid), and proportion of magnesium chloride, ammonium chloride, etc., present. In most cases, however, the differences are very small. The presence of potassium chloride in the solution causes the results to be too high owing to the inclusion of potassium in the precipitate. (See also *Jour. Chem. Soc.*, June, 1919.)

Dyeing and Finishing of Chrome and Semi-Chrome Leathers. By M. C. LAMB, *Leather Trades Review*, June 11, 1919. I purposely amalgamate chrome and semi-chrome because the operations which follow after tanning chrome and semi-chrome are practically identical and common to both classes of leather.

The first operation is simply the operation of washing when the goods have been tanned or retanned, as the case may be. They require to be washed with the object of removing the soluble salts and as much of the acid liberated in the process of tanning or retanning as is possible by washing in water. The washing operation is very important.

It was an operation which in the early days of chrome and semi-chrome tanning was very much neglected. The early pioneers who came over here with the object of teaching the leather trade the chrome industry were quite *au fait* with the necessity of washing the leather. To such an extent were they impressed with the importance of the operation that they washed the goods very often, I know in more than one case, for a period of 12 hours. The washing was carried out in one or two different ways. The American tanner often used to do it in running water for a long period, and he wondered often why he got irregular results. The irregularity was often caused by the variation in the quality of the water used. Water which contains a large quantity of temporary hardness will bring about a considerable variation in the leather.

Generally speaking, I think the washing is best done in a drum with hot water. Washing the goods at a temperature of 110° to 120° F. in two changes of water in a drum is the method which I think is to be preferred.

When the goods have been thoroughly washed they are ready for neutralizing. Neutralizing is equally as important as the washing. It has for its object the neutralizing of the acid resulting from the decomposition of the chrome salts in the process of tanning.

The acid can be neutralized with any suitable alkali. The most commonly used alkaline salt is borax. This was no doubt chosen in the early days of chrome tanning because of its weakly alkaline character and the non-liability of damaging the leather by the use of an excess. Viewed however, from the economy standpoint, and when the operation is in careful hands, a very considerable amount of money can be saved in the present day by the substitution of borax by other alkaline salts.

The saving that can be effected by the substitution of, say, sodium bicarbonate for borax amounts to no less than 2s. 3½d. for each 1,000 pounds weight of leather processed, while if substituted by soda ash the

cost is less than 2½d. per 1,000 pounds. The amount of borax used varies considerably in different operators' hands from as low as ¾ per cent. to as high as 3¾ per cent., and is dependent upon the degree of washing, the alkalinity of the water used, and the basicity of the liquor employed in the tanning or retanning.

It is essential that the goods should not be over neutralized even on the grain surface. Over neutralization has a tendency towards hardening the grain, and in extreme cases imparts brittleness to it and renders the leather more India-rubber like in character on account of increasing the basicity of the chrome salts on the fibers. Generally speaking, if the washing is not unduly prolonged in excessively temporary hard water, and the goods have been sufficiently well washed, the amount of borax necessary is in the neighborhood of 1 to 1½ per cent.

A sufficient amount of alkali has been used when, on removal of the goods, the solution still remains very faintly alkaline; the goods have been insufficiently neutralized when the solution left in the drum is acid.

After the goods have been neutralized the next operation is washing. Results from the neutralizing of the acid will get other soluble salts, which require to be removed again by washing. These soluble salts and acids cause spue on the surface of the finished leather, and they will also retard the penetration of the fat liquor and be troublesome in the dyeing process. The necessity for neutralizing the acidity is on account of the fact that unless it is removed, the acid will react upon the soap ingredient of the fat liquor, liberating the fatty acids on the surface, and the leather will spue white or greasy exudations when finished.

The uncomfortable feeling experienced by wearers of chrome boots in the early stages of chrome tanning was undoubtedly due to the insufficient removal of the soluble salts, and the insufficient neutralization of the acid before fat liquoring.

After the goods have been neutralized and washed, the next operation is dyeing. Time does not allow of my dealing with this very important subject in the thorough manner I should wish to. The great proportion of chrome and semi-chrome leather is dyed black. There are many different methods of producing this color on these leathers. Perhaps the most common method is to mordant the leather with extract of logwood (hematine) and to add either at the commencement or after the goods have been drummed for some little time a dyestuff for the purpose of imparting a characteristic color to the flesh side, and at the same time intensifying the black produced on the grain surface. Direct cotton blacks, which are commonly sold to the leather trade under the title of chrome leather blacks, nigrosine, induline, or where a bluish flesh is required, an acid violet is usually added to the logwood solution, the black color being subsequently obtained by the use of a "striker." Iron salts, or titanium salts may be employed for this purpose.

Under pre-war conditions undoubtedly the simplest and best methods of dyeing these leathers black was to first mordant with a small quantity of a weakly alkaline logwood, and with a view to accentuating the black,

adding a proportion of fustic extract. The amounts generally employed were 2 to 3 per cent. logwood (hematine) and ½ to 1 per cent. fustic extract (solid) to which sufficient ammonia was added to change the color of the logwood to a bluish-violet shade, using about 1-10 to 1-20 per cent. The goods were drummed in the natural dyestuffs mordant for about three-quarters of an hour at a temperature of 120° to 140° F., and then about 1 to 1½ per cent. basic black was added, and the drumming continued for half an hour.

This had the effect of producing an intense black grain and flesh, the color of the latter being modified if desired by addition to the basic black of either methylene blue or methyl violet. Unfortunately basic black is not available at the present time in any quantity, and the prohibitive price charged for the small parcels occasionally met with is such that the economic use of this dyestuff is impossible. Also fustic extract is not obtainable.

Probably the best and most economical method at the present moment is to dye the goods with a mixture of logwood extract and nigrosine, using 2 to 3 per cent. logwood, together with ¾ to 1 per cent. nigrosine in a drum, drumming for about three-quarters of an hour, until the solution is approaching exhaustion, and then add a "striker," using for this purpose a suitable iron salt, or, what is to be preferred, a titanium salt. Both these metallic salts produce bluish blacks with logwood. Iron, as is well known, is not altogether a satisfactory agent, on account of its liability to produce tightness in the finished leather, drawn grain, and a tendency to crackiness if used in excess, and it is for this reason that the substitution of this salt by titanium is to be preferred.

The amount of iron salt used should be the smallest possible to produce the desired results, and should not exceed ¼ per cent. Titanium (titox) up to about 1 per cent. can be used with safety. The metallic salt should be added to the contents of the drum, and the goods drummed for about 10 to 15 minutes, when they are preferably removed, horsed up for about one hour, rinsed through water, struck out, and may then be fat liquored.

Dealing with the colored chrome and semi-chrome leathers, the most common shades on these leathers are browns, which vary from the war-time color of tony red to a yellowish shade of tan brown. Shades of grey, navy champagne, ecru, are only common to glace kid.

The operation of dyeing consists in mordanting with a suitable tannin or dyewood mordant, and then dyeing with a selected mixture of coal tar colors. Of the latter, both acid and basic colors are employed. Whichever class is selected, the tannin mordant is essential. Pre-war, the mordant in universal use was gambier and fustic extract, but, as previously stated, the latter is now extremely scarce and of very high price.

For the production of brown "willow," the most satisfactory mordant is gambier, and the amount required is generally between 2 and 3 per cent. An excess is not to be recommended, because the retanning action of this

material has a tendency to tighten the leather and to detract from the soft, supple feel of chrome leather. The goods are drummed in the tannin mordant for a minimum of 30 minutes at a temperature of from 120° to 140° F. When the mordanting bath is approaching exhaustion, the dye stuff may be added. If the dye stuff used is a basic color there will be a slight precipitation in the dye bath of the gambier remaining in the used solution, but if the mordant has been properly proportioned and the drumming has been sufficiently long, the bath should be almost exhausted. In this case the loss occasioned by precipitation should be very little, but the labor involved in the removal of the goods and the refilling of the vessel with water, will be less economical though more scientifically satisfactory.

Acid colors are best developed by the addition of sodium bisulphate or formic acid; the quantity of either should be as small as possible, as both of these agents if used in excess are likely to produce difficulties in the fat-liquoring operation.

At the present moment it is extremely difficult to dye chrome leather in anything like as satisfactory a manner as under pre-war conditions, on account of the absence of suitable dyes. In dyeing brown, basic colors of the phosphine class give the most satisfactory results. These, however, are almost unobtainable, and have to be substituted by bismarck brown, chrysoidine, auramine, etc., mixtures. The first mentioned is not very satisfactory for dyeing, on account of its tendency to deposit itself on defective grain irregularly, particularly on the surface, and to exaggerate grain defects.

The acid brown dyestuffs on the market are also not very satisfactory, and consist principally of mechanical mixtures of orange, fast-red, yellow and nigrosine, or fast blue and other toning agents.

The quantity of basic color necessary to produce a full shade is in the neighborhood of 1 per cent., while almost double this quantity may be employed with advantage in the case of acid dyestuffs.

Fairly satisfactory browns can be produced by mordanting with gambier, using a titanium salt as a striker, in sufficient amount to produce a yellowish brown shade (say 1 per cent.) and topping off with a basic color, or using the acid dyestuff in the same bath as the titanium salt.

Tony red shades are produced with bismarck brown, either used alone or in conjunction with magenta or rhodamine, for the purpose of making the shade of a redder hue, or by mixing acid brown and fast red or roccelline.

Fat-liquoring.—The next operation is fat liquoring. This is perhaps one of the most important operations in the manufacture of these classes of leather. If the goods are over-fat-liquored, difficulties will be experienced in the finishing operations; if under-fat-liquored they will not be sufficiently nourished, and cannot be rendered soft and pliable. If the fat-liquor is not completely absorbed, the leather will be greasy on the surface and difficult to manipulate in the finishing. The most common practice in fat-liquoring is to add the fat-liquor in the form of an emulsion

to the used dye-bath after the leather has absorbed the greater proportion of the dyeing material. This practice is not to be recommended, except in the case of colored leathers. It is essential, in order to obtain complete permeation of the leather and subsequent perfect lubrication of the individual fibers, that the leather in the first instance should be in a semi-dry condition, and also that it should be warm. The fat-liquoring emulsion should not be used in large volume; only just sufficient should be used to insure a small pool at the bottom of the drum for the goods to fall into as the drum rotates; 2 or 3 gallons of the prepared fat-liquor emulsion for each 100 pounds leather is generally a sufficiency.

The best method of carrying out the operation of fat-liquoring, in my opinion, is in the case of blacks to remove the goods from the drum after dyeing, rinse in water, drain for one or two hours, strike out or press with a view to getting rid of as much superfluous moisture as possible, and then re-enter the goods into a drum which has been previously heated either by hot air, as in the case of using a hot air stuffing drum, or by means of blowing in live steam for 10 to 15 minutes with a view to getting the vessel as warm as possible.

The semi-dry goods are placed in the warm vessel and drummed for about 5 minutes to insure that they have become thoroughly warm throughout, then the fat-liquor emulsion is added, as I have just stated, in as concentrated a solution as possible, and at a temperature of not less than 140° F. The use of a small quantity of liquid in the drum insures a complete permeation and penetration into the leather, and at the same time it minimizes the liability of washing the color from the goods, which is always liable to take place when the solution is used in comparatively large volumes. When the goods are removed after fat-liquoring they should not be greasy on the surface. The absorption should have been thorough, and while the leather should possess a slightly slippery surface, there should be no globules of separated oil adhering to either the grain or flesh surfaces. With reference to the constituents of the emulsion to be used, it is, of course, a well known fact that, in the case of glace kid the most suitable fat-liquor emulsion contains as an ingredient a large proportion of neatsfoot oil. This is a very expensive product at the present time, and while there is not a really satisfactory substitute for this it may partially be substituted, with a view to minimizing the cost of the operation, by the use of a suitable sulphonated oil, or by a cheaper vegetable oil, such as cotton seed or olive oil.

In the case of chrome and calf side leather, and semi-chrome leather, castor oil, on account of its high lubricating property and heavy viscosity, is a suitable oil to use.

The fat-liquor emulsion usually consists of a mixture of soap (of which soft soap is to be preferred to hard soap) with the addition of oil.

During the last few years the employment of sulphonated oils has become more common. Sulphonated castor (Turkey red oil), sulphonated resin, mineral oil, and wood olein, have also been recommended for fat-

liquoring. Using a sulphonated oil as an emulsifying agent rather than as a lubricant itself, and introducing the latter desirable property by the use of neatsfoot oil, the result is a very satisfactory fat-liquor. Such sulphonated oil produces a better fat-liquor than a fat-liquor consisting of soap and oil. The further advantage is that the sulphonated oil fat-liquor is much easier to prepare, and there is not the liability of getting separation of the fat-liquor on the surface, as when soap is the emulsifying agent. On the other hand, the soap acting as a filling agent conduces to greater plumpness than is the case when sulphonated oil is used as a substitute.

The amount of fat-liquor required is determined to a considerable extent by the thickness of the leather and the ingredients. Generally speaking, 3 to 4 per cent. of oil on the weight of semi-dry leather is necessary; the proportions may be varied to suit individual requirements, and may consist of either neatsfoot oil, castor oil, olive oil, wool olein, or degras. The sulphonated oil for chrome leather is a sulphonated wool olein, or sulphonated mineral oil, and requires to be selected with care. Sulphonated resin oil is not to be recommended. When the goods have been fat-liquored they should be removed from the drum, and horsed up for 24 hours before striking out preparatory to drying. Allowing this period of time to elapse before the goods are dried, enables the fat-liquor to enter into more intimate combination with the fibers, and is consequently not so liable to be removed in the striking out operation. The drying may be carried out at a comparatively high temperature, and should be done quickly. When dry the goods should be stacked for several days in a cool atmosphere to enable them to absorb a little moisture and become more mellow, when they are ready for damping, preparatory to staking. Damping is either done by spraying with water and subsequently stacking in pile covered over with a waterproof sheet, or by dipping in cold water and stacking in a similar manner, or what, perhaps, is more common, stacking in previously damped sawdust. When in a suitable moist condition they are staked, dried, re-staked and seasoned preparatory to glazing. The seasoning mixture consists of egg or blood albumen, or blood, in conjunction with a dyestuff and a lubricating agent in the form of an emulsion. The goods are seasoned, and after seasoning they are dried and glazed, and, in the case of box sides, grained and finished by oiling with a thin mineral oil.

I should like to take this opportunity of addressing a few remarks relative to the leather which has been retanned with chrome salts, and is commonly termed "semi-chrome." This leather, during the last few years, has not been popular among boot manufacturers, whereas between the period 1899-1914 it provided the largest proportion of boot upper material manufactured in Great Britain. It might, perhaps, be interesting to advance an opinion as to the primary reasons for its decline in popularity and to point out what has occasioned this. In the early part of 1899, when American box calf made by the chrome process was exported to this country in large quantities, and British tanners of calf kid and other

leathers were engaged in experimenting in the manufacture of chrome calf, there was a consequent decline in popularity of wax kips and wax calf, and the shoe leather currier, who had been primarily engaged in the dressing of vegetable-tanned calfskins for boot upper leather, began to have a feeling of uneasiness that chrome tanning would eventually supplant the leather that he was then producing, and that the major part of his vocation would be taken from him. Experiments were made by several firms in the direction of re-tanning vegetable-tanned leather, with the object of imparting to it the characteristics of a Dongola or chrome leather. One of the earliest patents for this process was one taken out by the late Mr. George Whichelow, who treated vegetable-tanned East India goats with an alum solution, with the object of producing a glace leather, which was to be an improvement on a glazed vegetable-tanned goat. It suggested itself, about this time, that it might be practicable to remove part of the original tannage from a lightly tanned leather like an East India kip or East India tanned Persian by means of a weak alkaline solution, and to subsequently re-tan it with a basic solution of a chrome salt, and a large number of experiments were carried out with this end in view. I well remember my early experiments in this direction, and the scornful remarks passed upon the product produced, by those to whom it was shown. It was criticised from the point of view of extra cost and being neither a vegetable tannage nor a chrome tannage, and possessing defects common to both. Pursuing these experiments, a result was at last obtained which was considered sufficiently satisfactory to warrant several leather dressers trying the manufacture on a larger scale. The method which was eventually commonly adopted was to strip the vegetable-tanned leather lightly by treatment with a weak alkaline solution of washing soda and then re-tan with chrome alum, rendered basic by the addition of an alkaline carbonate. It was found that the leather, due to the presence of the tanning mordant, was capable of the absorption of a greater amount of chromium salt than was commonly found to be present in a pure chrome-tanned leather. This leather, properly prepared, had certain chrome characteristics as regards softness, ability to withstand the action of boiling water without becoming damaged, and possessed a softness, suppleness, and feel not common to the purely vegetable-tanned product, and subsequently the process was used on a fairly considerable scale, particularly in connection with the manufacture of brown tan colored calf.

About 1905, or perhaps a little earlier, the manufacture of side leather from East India tanned kips, glazed and boxed on the grain, became very common practice. Competition in this leather became very keen, and every manufacturer's endeavor was to cut down the cost of production, with the consequence that many of the so-called semi-chrome leathers on the market contained the smallest possible amount of chrome salts. East India tanned kips are in normal times only lightly tanned, and are, as is well known, commonly often quite green in the center of the thickest parts. To remove the tannin by treatment with borax, washing soda, or other alkali, and not to replace the same by chrome or other tanning

material, is only courting failure from the point of view of the wearing property of the finished leather. There is no reason why leather thoroughly re-tanned with chrome should not possess the wearing property of real chrome leather, but it is essential that, in order to obtain this desired result, the leather should possess a chromic oxide content of a minimum of 2.5 per cent. on the weight of dry leather. The method of dressing this leather is somewhat varied, but in general the process is carried out as follows: The goods, after shaving, are placed in the drum with water which must not exceed 95° F. After a thorough wetting the addition of a suitable quantity of an alkali is made, the alkalies used being borax, washing soda, crystal soda, or soda ash. After solublizing a portion of the vegetable tanning material and the grease present in the leather by this means, the goods are washed. The washing operation is extremely important. The action of the alkali is, as just stated, to remove the tannin and to convert the grease (natural or added) present in the leather, into soap. If the goods are re-tanned without washing, the acid liberated during the process of re-tanning with chromium sulphate or chromium chloride has the effect of precipitating the tannin from the sodium tannate, formed by the action of the alkali on the vegetable-tanning material of the leather, and also liberating the fatty acids from the soap solution which has resulted from the action of the alkali on the oil and fatty matter of the skins. This will have the effect of rendering the work that has been done by the weak alkali of no avail, and at the same time it will conduce to subsequent irregularity in dyeing, be liable to produce difficulties in the finishing operations, and also minimize the chrome leather-like characteristics of the resulting product. When stripped and washed, the goods are now re-tanned. The re-tanning is best done in warm solution at a temperature not exceeding 95° F. The chrome liquor before the war was commonly prepared by rendering chrome alum basic by the addition of washing soda or other alkaline carbonate. The liquors now employed are prepared by the reduction of acidified bichromate with glucose or other organic reducing agent, or are bought ready prepared. The goods are placed in sufficient water and the chrome liquor added in one or more portions, and the goods drummed for a period varying from half an hour to two hours, when they are usually removed, horsed up for a few hours, and are then ready for washing and neutralizing, the subsequent treatment being almost on identical lines to that of real chrome leather. It seems a pity that semi-chrome leather, which can be manufactured in very large quantities indeed from imported East India kips as a substitute for box calf and chrome box side leather, should be allowed to remain under the present stigma, and be in danger of being relegated to the past, when the present method of dressing is capable of improvement, and the production of a leather which will give satisfaction in wear.

I have recently been experimenting with a view to improving the manufacture of this leather from the above-mentioned standpoint, and also to speed up and to economize the process of manufacture. One of the chief objections from the standpoint of the manufacturer of this class of

leather in the past has been the numerous operations through which the leather had to be processed from the time of shaving to that of drying, numbering no fewer than ten separate and distinct processes, and necessitating in some cases the handling of the goods four or five times.

The following method will be found to be a great improvement on the process just described. The goods, after shaving, are weighed, and are then transferred to the drum with a sufficiency of water to make a comfortable float, at a temperature of 95° F. After drumming for a period of about 10 minutes to insure the leather being thoroughly well wetted throughout, the alkaline salt used for stripping is added. It is, of course, obvious that the larger the amount of alkali used, the greater the stripping action, and the more re-tanning will be necessary when the goods come to be chromed. On the other hand, the greater the amount of vegetable tannin removed from the leather, the nearer resembling real chrome will be the finished article. The alkali most commonly employed in the stripping of the leather is borax, but at the present time, on account of the high price of this material and the fact that it is not nearly so effective as the stronger alkaline carbonates, it is to be recommended that this salt be substituted by the use either of sodium bicarbonate, washing soda, or soda ash. An amount of soda ash which will generally be satisfactory is about ½ per cent. on the weight of shaved leather. The goods are drummed in the alkaline solution for a minimum of 30 minutes. The solution should then be run off, and replaced with clean water, preferably at a temperature of 95° F., and the goods drummed for a further period of 10 to 15 minutes.

It is to be recommended for the purpose of convenience to have a drum provided with a supply of running water, replacing the door of the drum with a latticed door; the goods can then be washed in the running water until it is obvious that the wash water is quite clear, which is an indication that the whole of the solublized tannin has been effectually removed. The drum should then be run up with water again, and the chrome solution may then be added. The most satisfactory semi-chrome leather should contain between 2 per cent. and 3 per cent. chromic oxide on the dry weight of finished leather. The latter figure is the amount usually found to be present in a real chrome-tanned leather.

The quantity of a reduced chrome liquor acidified with the requisite quantity of sulphuric or hydrochloric acid, and then reduced with an organic reducing agent, such as glucose, glycerine, or starch, etc., and containing 3 pounds sodium bichromate per gallon of the liquor, or in the case of bought liquor, ready prepared containing 15 per cent. chromic oxide by volume, required to effect this result will be 2 gallons for each 100 pounds of dry leather. The chrome liquor may, with advantage, be added in two portions; adding half at the commencement and the remaining half after half hour's drumming. At the end of about 60 minutes drumming, when the liquor should be approaching exhaustion, a quantity of washing soda or sodium bicarbonate should be added—sufficient in amount to reduce the original basicity of the liquor to 70. The quantities to effect this result are given as follows:

Original basicity figure	Final basicity figure	Amount washing soda required per 2 galls. liquor	Amount sodium bicarbonate (100 per cent.) required per 2 galls. liquor
80	70	1.23	1.7
90	70	2.46	1.4
100	70	3.69	2.1

The degree of basicity of the chrome liquor in the tannage of semi-chrome leather is almost as important as in chrome leather tanning.

The object of adding washing soda or sodium bicarbonate is to increase the basicity of the liquor in the goods and to neutralize the acid liberated in the retanning process. After the addition of the alkali the goods should be drummed for about a half-hour. They may then be washed, dyed, and fat-liquored without resorting to the operation of neutralization. The increasing of the basicity of the chrome salt in the process of tanning has the effect of making the leather more chrome-like in character, and at the same time more firmly fixing the chrome salt on the fibers of the leather. The leather after drumming for the period stated should be thoroughly "chromed" and capable of withstanding immersion in boiling water without shrinking, which, as I have previously explained, is the test which good semi-chrome leather should always satisfactorily stand.

The Volumetric Determination of Sulphurous Acid. By THOS. J. I. CRAIG, *J. S. C. I.* 38, 96T (1919). The method described in this paper depends on the following reactions:

(1) $SO_2 + H_2O_2 = H_2SO_4$;

(2) $5H_2O_2 + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$.

The sulphurous acid (also sulphite or bisulphite) in solution in water is added to a known excess of acidified hydrogen peroxide and the residual hydrogen peroxide is determined by titration with standard permanganate.

Samples of sodium sulphite, potassium meta-bisulphite, and commercial sodium bisulphite liquor were employed to test the method. It was found that the action of hydrogen peroxide on sulphur dioxide is best carried out in a solution which is not too dilute; afterwards the liquid may be diluted before titrating back with permanganate.

Proposed Method. 1 gram of the sample is dissolved in from 25 to 50 cc. of distilled water and gradually added to a decided excess of standardized hydrogen peroxide—an excess equal to about 10 cc. of N/2 permanganate should suffice. The amount of hydrogen peroxide taken is noted and stated as its equivalent in cc. N/2 solution—say x cc. 10 cc. of dilute (1 : 3) sulphuric acid is now gradually run in and the whole well mixed. The mixture is cooled to ordinary temperature and the residual hydrogen peroxide determined by titration with N/2 permanganate. The volume of the permanganate used is noted = y cc. Then $x—y$ = cc. of N/2 permanganate equivalent to the sulphur dioxide present in the portion taken for analysis.

Since sulphites and bisulphites in dilute neutral or acid solution rapidly deteriorate, as short a time as possible should be allowed to elapse between dissolving the sample in water and adding it to the hydrogen peroxide. Alkaline sulphite solutions do not deteriorate so quickly. The hydrogen peroxide solution is standardized by titrating 10 cc. (of "10 volume" solution) with N/2 permanganate under conditions similar to those in which the analysis is made.

RESULTS. *Potassium Metabisulphite.* Five-tenth gram was treated with 10.2 cc. of hydrogen peroxide. $x—y = 14.5$ cc. = 80.22 per cent. $K_2S_2O_5$ Another test similarly carried out, but using 6.8 cc. of hydrogen peroxide, gave the same result. Comparative tests made by another chemist using the iodine method gave 80.10 per cent., 80.21 per cent. and 80.32 per cent. $K_2S_2O_5$.

Potassium Metasulphite Crystals. By iodine 90.5 per cent. and 90.5 per cent. $K_2S_2O_5$. By author's method 90.41 per cent. and 90.37 per cent.

Sodium Sulphite Crystals. By iodine method 90.91 per cent. and 90.85 per cent. Na_2SO_3, $7H_2O$. By author's method 90.97 per cent. and 90.72 per cent.

Sodium Bisulphite Liquor. By iodine 12.71 per cent., 12.70 per cent. and 12.72 per cent. SO_2. By author's method 12.73 per cent. and 12.72 per cent. References to bibliography are given.

The Tannin Content of Redwood. By CHARLES C. SCALIONE and DAVID R. MERRILL, *J. Ind. & E. C.* 11, 643 (1919). The rapid depletion of the more accessible supplies of tanbark oak (*Pasania densiflora*), which is the only natural source of tannin largely utilized on the Pacific Coast, suggested the desirability of a study of the wood of the coast redwood (*Sequoia sempervirens*), which is known to contain tannin and of which a large supply is available in the form of refuse from the lumber industry.

With this idea in view, samples of bark, heartwood, and sapwood were obtained from Mendocino County. The bark was shredded and ground in a mill to pass a 20-mesh screen. Samples of the heartwood and sapwood were prepared by sawing, and grinding the sawdust to pass 20 mesh. The moisture contents were determined by drying samples to constant weight. The undried samples were extracted by soaking them for several hours in warm water, pouring off this extract, and extracting the residue with more water in an extractor of the Soxhlet type. The extraction was stopped when the extract gave a negative test with the salt gelatin reagent for tannin. The mixed solutions were diluted to volume and clarified by adding washed kaolin and sucking them into a flask through an alundum extraction thimble. After this treatment the samples passed the requirements for optical clearness as given in the A. L. C. A. specifications.

The following results were obtained using the A. L. C. A. hide-power method. The results are calculated to a dry basis in each case.

	Bark Per cent.	Sapwood Per cent.	Heartwood Per cent.
Soluble solids	2.76	4.77	25.7
Non-tannins	1.89	3.62	13.5
Tannin	0.86	1.15	12.2

It is evident from these figures that the only part of the redwood which has any possible value as a source of tannin is the heartwood. The principal source of raw material here would be the sawdust. The proportion of soluble non-tannins is high, which is in part due to the method of extraction used. The extract gave a qualitative test for pyrogallol derivatives. The liquors were quite dark from the coloring matter which occurs in the redwood. A sample tanning was run on some strips of hide. The grain developed quickly and struck through in about four days. The outside of the hide was colored a dark purplish brown, but the color did not penetrate through the hide. For heavy sole leather this material might be satisfactory.

Another possible source of tannin from redwood is in the liquor which collects on steam-kilning the wood. While a quantitative analysis of these liquors was not made, they appeared to contain about 7 to 10 per cent. tannin when the salt gelatin test was made. In the same connection it should be noted that Scalione and Blakemore[1] found that the leaves of *Ceanothus velutinus* were quite rich in tannin. This shrub covers a large acreage in certain regions of California and could be collected in large quantities at but small cost.

PATENTS.

Machine for Treating Hides and the Like. U. S. Patent 1,300,920. C. P. Bossert, Milwaukee, Wis. An apparatus for applying substances to hides and the like, having means for delivering the substance to a position adjacent the hide, a flexible strip for receiving a portion of the substance therefrom, and means for moving said strip at a comparatively high velocity to throw the substance received thereby onto said hide.

Feeding Device for Bark-Stripping Machines. U. S. Patent 1,301,200. W. Waern, Stockholm. A feeding device for bark-stripping machines and the like which are provided with a rotating feeding roller arranged at an angle relatively to the trunk and by means of which the trunk is rotated at the same time as it is moved lengthwise.

[1] This Journal, 8, 411, (1916).

Bark-Rossing Machine. U. S. Patent 1,306,869. J. W. VANDERVEER and W. L. LYNCH, Liverpool, N. Y. A bark-rossing machine comprising branch gripping means, bark stripping means, a carriage movable horizontally, one of said means being carried by the carriage, the gripping means and the stripping means having an opening and closing movement in horizontal directions at an angle to the traveling movement of the carriage, the jaws being arranged so that when open, unobstructed space is provided below the jaws, and means supporting the jaws arranged out of the vertical plane in which the branch is located when held by the jaws whereby the branch and bark when released fall by gravity, mechanism for opening and closing said means, and driving means for the movable parts of the machine, substantially as and for the purpose specified.

Preservative for Leather and Leather Substitutes. U. S. Patent 1,307,059. L. A. MILNE, Fresno, Cal. Consisting of seventy-five parts of crude mineral oil gas tar, and twenty-five parts of gum copal varnish, thoroughly mixed.

Tanning. British Patent 123,448. J. WRIGHT. Hides are suspended from trollies which are lowered by winches until the hides are immersed in the pits. The trollies are again raised by a winch and each trolley is then moved forward by another winch until it is over the next pit, whereupon the hides are again lowered. The trollies are removed from the rails in succession when they reach the upper end of the run.

Leather Making. British Patent 123,785. E. MEYZONNIER, Annonay, Ardéche, France. Basic chrome salts for use in tanning are obtained by treating alkaline bichromates with sodium sulphite and an acid, and subsequently with additional sodium sulphite. The sodium sulphite employed may be the residual product in making phenol from benzene sulphonic acid, and the acid may be sulphuric obtained from gun powder works. Hydrochloric acid may also be used.

Hide-working Machines. British Patent 124,214. L. P. MORIN, Seine, France. A machine for whitening and paring skins or hides.

Tanning. British Patent 124,992. A. N. WALKER. Vats for soaking, liming, tanning, chroming, leaching, and like treatment of hides, etc., are arranged with a central dividing partition having its upper edge below the surface of the liquid and an opening or openings at the bottom. The liquor is caused to circulate by air or gas forced through pipes.

Tanning. British Patent 125,362. L. DUFOUR and G. DUFOUR, Genoa, Italy. March 1, 1919. Hides, etc., are unlimed or tanning liquors are reduced or prevented from oxidizing by passing a current of sulphur dioxide through the agitated liquid containing the hides.

Dyeing. British Patent 125,093. F. COCHRANE. Textile fabrics are dyed in such manner as to appear invisible when viewed from a distance, by first padding in a solution of a dye capable of producing two or more colors by after-treatment with metallic salts, then developing a uniform ground shade by means of a suitable metallic salt, and then applying other suitable salts, by hand or otherwise, in promiscuous patches to develop one or more further shades upon the ground. In an example, the fabric is padded in a solution of cutch, fustic, or sumac, the ground shade is then developed by passage through a bath of aluminium salt, and then bichromate of potash and iron salts are applied in promiscuous patches; the fabric is then folded and allowed to stand to allow the shades to blend, and is finally dried.

Journal of the

American Leather Chemists Association

Vol. XIV SEPTEMBER, 1919 No. 9

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Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $6.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized July 16, 1918.

A CHROME LEATHER CURIO.

At the Sixteenth Annual Meeting of the A. L. C. A. President Griffith exhibited a unique specimen of chrome leather that had been kindly sent for the occasion by Mr. Alfred Seymour-Jones. The specimen was produced at a tannery in Wales.

A piece of hide had become detached, and had jammed itself between the shelf and the outside of the drum in which the tanning took place, and successive chrome liquors, of the two-bath process passed through the drum. It isn't known how many liquors the

piece of hide received, but after some months it was noted that the hides coming out of the drum were scratched on the grain. That led to an investigation of the interior of the drum, with the result that this piece of what might be called chrome leather was discovered. It was originally pure hide. Three-quarters of it now looks more like a mass of metal, or a clinker, but by careful examination one could see that the grain of the original hide was still visible, and the fold of the hide was still in evidence. It seems that the hide has a tendency to revert to the metallic state. Mr. Griffith stated that some years ago he had the privilege of examining a piece of vegetable-tanned leather that had been laid away in vegetable liquor for something like 100 years and the leather looked more like wood than anything else.

Mr. J. B. Churchill was provided with a minute sample and it was found to contain 25 per cent. of chromic oxide.

THE PROPOSED ORGANIZATION OF AN AMERICAN STANDARDS ASSOCIATION.*

By L. M. Whitmore

A conference to consider the formation of a series of industrial codes was called by the Bureau of Standards to meet in Washington on January 15th. This conference was attended by over one hundred delegates from Federal, State and Municipal Departments, engineering and utility associations, and other organizations. The conference considered the best methods for the development of safety codes and other standards. Opinions were expressed to the effect that, in order to enlist the active support of all concerned and give maximum weight to the results, the development of such codes should be in the hands of a comprehensive and representative body of all those interested.

The plan of operation involves an elaboration of the present Engineering Standards Committee. This Committee was founded by joint action of the five engineering societies American Society of Civil Engineers; American Institute of Mining Engineers; American Society of Mechanical Engineers; American Institute of Electrical Engineers, and the American Society for Testing Materials to meet the need for some authoritative machinery for

* Read at Annual Meeting of the *A. L. C. A.*, May 24, 1919.

the development of industrial and engineering standards; by the operation of which duplication would be avoided and co-operation between all interested organizations secured, so that when a standard is developed, it will be acceptable to all concerned and therefore a real standard. Provision is made to have three Government departments represented. Such committees are already in operation in England, Canada, France, and Holland, and international standardization is developing.

The general proposition was discussed at several subsequent conferences, and was finally considered on April 12th, at a meeting of the American Engineering Standards Committee at which representatives of the fire-protection and safety interests, the Federal Government, and other organizations were present. It was unanimously voted by the Committee to ask the five founder societies to amend the constitution so as to permit the admission on an equal basis of other organizations or Government departments interested in standards. The general sentiment was favorable to a large increase in the membership of the Committee, and it was voted to recommend to the founder societies that the name be changed to the American Engineering Standards Association. it is expected that these changes will be approved by the founder societies in the near future.

In view of the above action of the Committee, it seems that it would be better for the various interested bodies to join the organization as soon as the changes in the constitution make that possible. It is, however, *not necessary* for an association to be represented in the Committee before submitting its standardization work to the Committee for approval.

When the development of any group of standards is proposed the main committee assigns the work to the appropriate organization or organizations. This sponsor body then appoints a committee, subject to the approval of the main committee. After a group of standards has been prepared by this committee, it is submitted to the sponsor body for approval, and then to the main committee with a full report of its history. If approved by the sponsor body and the main committee, the standard is published by the sponsor body with the statement that it has been approved by the Engineering Standards Committee and labeled "American Standard."

At present there are three grades of standards:

Tentative Standards,
Recommended Methods of Procedure,
Standards.

Should the A. L. C. A. desire to have its official methods of analysis made the American Standard (of any of the three grades) they would form a committee representing all parties interested in the analysis in question. When the methods were approved by this Committee, they would be submitted to the American Engineering Standards Committee for approval as American Standard. They would then be published as at present, but with the statement that they had been approved by the Committee and were American Standard. This would give the official methods more weight, as they would then be officially adopted by the whole country, as represented in the American Engineering Standards Committee. Revisions would go through the same procedure, and upon approval would supplant the methods formerly approved.

NOTES ON THE DETERMINATION OF WATER SOLUBLES IN LEATHER.*

By R. W. Frey and I. D. Clarke.

It is gratifying to note that more interest is being aroused in the methods for the analysis of leather, a subject which has not received its due share of attention. With commodities that might be called ideal for chemical analysis discordant results are not uncommon while with leather, an article of a very complex, organic nature and of little understood formation, they are unpleasantly frequent. For this reason alone the methods for the analysis of leather should be standardized in detail and any information that throws light upon even an apparently insignificant point, or that inspires constructive interests in the methods, should be welcomed.

One of the constituents in the composition of at least certain types of leather that has come into prominence lately is water soluble matter. The present brief and rather indefinite directions

*Read at the Atlantic City Meeting of the A. L. C. A., May 23, 1919.

for determining this constituent were embodied provisionally in the A. L. C. A. methods at least as early as 1908 and they have remained to date intact in spite of the committee work under Hoppenstedt,[1] Veitch,[2] and others, showing the discordant results obtained, and the conclusions that the method for determining water soluble should be further investigated. Very recently J. A. Wilson in his committee report on "The Extraction of Grease and Oils in Leather"[3] incidentally called attention to the need of more work on the method for determining water solubles in leather.

Some data having been obtained on this determination it is given here as being of possible value to others and with the hope of arousing interest.

Need of Over Night Soaking Before Extraction.

A member of the Association has stated that preliminary results he had obtained indicated that soaking the leather over night as required by the official method was unnecessary. It was suggested that more data on this point would be desirable and during the course of the regular work of the leather and paper laboratory a comparison was made of these two procedures, that is, soaking over night and not soaking. By soaking is meant, allowing the weighed sample of leather to stand over night in a beaker at room temperature with sufficient water to thoroughly wet and just cover it.

The apparatus used for the extractions is a more or less temporary one, made during the emergency. It consists essentially of a rectangular tank as a bath in which the water is heated by a steam pipe. Distilled water supplied from an overhead vessel, passes through a copper coil in the water bath and then up through small copper outlet tubes from which it drips on to the leather contained in alundum thimbles having perforated bottoms. The alundum thimbles are in turn supported in suitable shaped glass tubes the ends of which pass through the bottom of the water bath and have attached to them siphon tubes. The top of the siphon is slightly above the level of the leather in the extrac-

[1] This Journal, Vol. 3, 255.
[2] This Journal, Vol. 4, 272; Vol. 5, 129, 426, 532; Vol. 7, 91.
[3] This Journal, 14, 140.

tion thimble. An apparatus of this type is, therefore, based upon extraction by siphoning instead of percolation.

The apparatus was originally designed to accommodate twenty samples but it was found that the temperature variation from one end of the bath to the other was too great, so that one-half of the apparatus was partitioned off and when provided with a paddle stirring device no difficulty was experienced in controlling the temperature of the bath well within 0.5° C.

TABLE I.—COMPARISON OF WATER SOLUBLES OBTAINED BY SOAKING OVER NIGHT AND BY NOT SOAKING.

L. & P. No.	Description	Preparation	Water solubles soaked over night Per cent.	Water solubles not soaked Per cent.	Difference Per cent.
34334	Oak	Shredded	24.3	24.7	+0.4
34523	Oak	"	23.9	23.9	0.0
34528	Texas bloom	"	26.4	26.9	+0.5
34543	Union	"	24.5	25.7	+1.2
34552	Union	"	21.8	22.5	+0.7
34554	Oak	"	22.0	22.1	+0.1
34559	Union	"	26.0	26.1	+0.1
34561	Oak	"	21.2	21.3	+0.1
34566	Union	"	23.9	24.5	+0.6
34569	Union	"	26.2	26.5	+0.3
34576	Texas bloom	"	21.5	22.0	+0.5
34579	Oak	Planed	15.7	15.5	—0.2
34582	Union	Shredded	22.9	22.9	0.0
34585	Union	"	22.7	23.0	+0.3
34586	Union	"	17.5	17.5	0.0
34588	Hemlock	"	24.2	24.4	+0.2
34591	Hemlock	"	29.0	29.0	0.0
35362	Union	"	24.6	25.0	+0.4
35437	Hemlock	"	24.0	23.4	—0.6
35447	Hemlock	"	25.1	24.9	—0.2
35454	Union	"	24.7	23.7	—1.0
35460	Union	"	28.5	27.7	—0.8
		Average	23.6	23.8	—

Since it is believed that the procedure which has always been used in this laboratory for charging the extraction thimbles differs slightly from the one commonly followed, it is probably well to briefly mention it. The weighed leather is placed in a beaker and thoroughly mixed and wetted with sufficient water, before transferring it to the extraction thimble. While this requires more time and manipulation than placing the dry leather directly in the extractor it is nevertheless believed advisable since it insures thor-

ough wetting of the leather and less chance for channeling and incomplete extraction.

The data obtained from the comparison of soaking and not soaking are given in Table I. Twenty-two samples of sole leather, embracing according to the trade designations, oak, union, and hemlock, were used.

The agreement in most cases is good and the difference between the averages for all the extractions by the two modifications is only 0.2 per cent. showing that both procedures give practically the same result. By omitting the over night soaking or digesting a sometimes desirable saving of time can be accomplished, to say nothing of the elimination of the possibility of the soaked leather and resulting solution undergoing change while standing over night under certain conditions.

This work aroused further interest in the determination of water solubles and the influence of several other factors was investigated. In all of the following experiments, unless it is otherwise specified, the samples were soaked over night and extracted by siphoning, with the bath maintained at 50° C.

Influence of Temperature of Extraction.

While it is well known that temperature will affect the extraction little data has been given to show to what extent variations will influence the results by the present method. The results in Table II were obtained by extracting 30 grams of the same leather with the bath at 45° C., 50° C., and 55° C., respectively.

The results show an average increase of 0.9 per cent. water solubles for 5° C. rise in temperature for the range 45° C. to 55° C. It should be stated that the temperature in the thimbles during these extractions was found to be always 3° to 4° C. lower than that of the bath and while this condition may cause the absolute values to be questioned, the relation or comparison still holds good. In view of this, the temperatures for this experiment should strictly speaking, be stated as 42° C., 47° C., and 52° C., respectively.

Influence of Rate of Extraction.

All the present types of extraction apparatus for water solubles in leather require hand control and regulation of the flow of

TABLE II.—INFLUENCE OF TEMPERATURE ON EXTRACTION OF WATER SOLUBLES.

L. & P. No.	Description	Preparation	Per cent. water solubles by extraction at		
			45° C.	50° C.	55° C.
34334	Oak	Shredded	23.0	24.2*	25.0
34523	Oak	"	22.9	23.7*	24.8
34526	Oak	"	27.2	27.9	28.5
34528	Texas bloom	"	25.3	26.4*	27.1
34536	Union	"	22.6	23.2	23.5
34543	Union	"	24.4	24.8*	25.4
34552	Union	Planed	18.9	19.8	21.0
34552	Union	Shredded	20.8	22.0*	22.8
34561	Oak	"	19.5	21.1*	21.6
34566	Union	"	23.7	24.1*	24.9
34570	Union	Planed	19.3	21.0	22.9
34585	Union	Shredded	21.8	22.7*	23.6
34588	Hemlock	"	23.9	24.2*	25.0
34591	Hemlock	"	27.8	29.1*	29.8
		Average =	22.9	23.9	24.7
	Average	difference =	—	1.0	0.8

* Averages of the results from the regular procedure in Tables I and IV.

water and it is believed, from the experience of this laboratory and from the informal statements of others, that this factor is not easily controlled. It therefore was deemed advisable to obtain some data on the effect of extremes in the rate of flow of the water. Portions of the same leather were extracted according to the two following modifications: first, with the rate of flow speeded up to give 1 liter during the first hour and then slowed down to give the second liter in 2 hours; and second, with the rate of flow adjusted to give 1 liter during the first 2 hours and then increased to 1 liter for the last hour. The comparison of the two procedures for each sample was always made at the same time. The results so obtained are given in Table III.

These figures show a surprisingly good agreement and indicate that variations in the rate of flow have very little effect provided the required volume of extract is collected in the specified 3 hours.

Siphoning vs. Percolation.

The official method does not specify whether the extraction shall be made by siphoning or by percolation, although it does imply the latter since it reads "Digest 30 grams of leather in a percolator over night, then extract with water at 50° C. for 3

TABLE III.—INFLUENCE OF RATE OF EXTRACTION ON WATER SOLUBLES.

L. & P. No.	Description	Preparation	1st liter in		2nd liter in		Total for		Differenec Per cent.
			2 hours A Per cent.	1 hour B Per cent.	1 hour C Per cent.	2 hours D Per cent.	Slow and fast A + C Per cent.	Fast and slow B + D Per cent.	
34334	Oak	Shredded	21.3	21.0	2.9	3.5	24.2	24.5	0.3
34523	Oak	"	20.8	21.5	2.6	2.4	23.4	23.9	0.5
34527	Oak	"	21.9	20.2	2.4	3.8	24.3	24.0	0.0
34528	Texas bloom	"	22.6	22.9	3.0	3.2	25.6	26.1	0.5
34543	Union	"	21.9	21.3	2.6	2.9	24.5	24.2	0.3
34552	Union	"	18.4	18.3	2.6	3.2	21.0	21.5	0.5
34561	Oak	"	18.6	17.9	2.5	3.1	21.1	21.0	0.1
34566	Union	"	21.8	21.3	2.2	3.5	24.0	24.8	0.8
34578	Oak	"	15.8	15.2	2.8	3.3	18.6	18.5	0.1
34585	Union	Planed	19.7	19.0	2.3	3.0	22.0	22.0	0.0
34585	Union	Shredded	20.0	20.3	2.7	3.0	22.7	23.3	0.6
34586	Union	Planed	15.6	13.9	2.0	2.8	17.6	16.7	0.9
34588	Hemlock	Shredded	22.6	21.6	2.1	2.3	24.7	23.9	0.8
34591	Hemlock	"	26.4	26.0	2.1	3.6	28.5	29.6	1.1
34668	Union	Planed	22.5	21.7	2.1	2.8	24.6	24.5	0.1
		Average	20.66	20.14	2.46	3.10	23.12	23.24	

TABLE IV.—COMPARISON OF SIPHONING, PERCOLATION, AND IMMERSED PERCOLATION.

L. & P. No.	Description	Preparation	Water solubles					
			Siphoning Per cent.	Percolation Per cent.	Deviation Per cent.	Siphoning Per cent.	Immersed percolation Per cent.	Deviation Per cent.
34334	Oak	Shredded	24.1	24.4	+0.3	24.0	23.9	—0.1
34523	Oak	"	23.4	24.0	+0.6	23.9	23.2	—0.7
34528	Texas bloom	"	26.4	26.5	+0.1	26.4	25.2	—1.2
34530	Texas bloom	"	—	—	—	26.4	24.6	—1.8
34534	Oak	"	—	—	—	22.1	21.1	—1.0
34535	Union	"	—	—	—	22.3	21.5	—0.8
34543	Union	"	24.8	25.2	+0.4	25.0	24.3	—0.7
34551	Union	Planed	—	—	—	21.0	20.4	—0.6
34552	Union	Shredded	21.9	22.1	+0.2	22.1	20.4	—1.7
34561	Oak	"	20.9	21.3	+0.4	21.3	19.8	—1.5
34566	Union	"	24.4	24.7	+0.3	24.0	23.3	—0.7
34568	Union	Planed	—	—	—	24.6	22.4	—2.2
34573	Oak	Shredded	—	—	—	23.0	23.2	+0.2
34575	Union	"	—	—	—	28.7	28.5	—0.2
34581	Union	"	22.5	22.7	+0.2	—	—	—
34584	Union	"	27.7	28.3	+0.6	—	—	—
34585	Union	"	22.8	23.2	+0.4	22.7	22.5	—0.2
34588	Hemlock	Planed	24.2	24.3	+0.1	24.3	23.8	—0.5
34588	Hemlock	Shredded	24.3	24.6	+0.3	24.1	24.1	0.0
34589	Union	"	26.4	27.3	+0.9	—	—	—
34591	Hemlock	"	29.2	29.2	0.0	—	—	—
34666	Union	Planed	16.2	16.2	0.0	—	—	—
34671	Union	"	24.3	24.1	—0.2	24.5	21.7	—2.8
34719	Union	Shredded	29.4	30.1	+0.7	—	—	—
34970	Union	"	23.9	24.4	+0.5	—	—	—
35005	Hemlock	"	27.0	28.3	+1.3	27.8	27.4	—0.4
		Average	24.4	24.8	+0.4	24.1	23.2	—0.9

hours." Furthermore there are what might be termed two different types of percolation. The first, in which a drop of solvent is free to pass through the charge, and the second, in which the charge is totally immersed in the solvent and as a drop of extract is removed a drop of solvent is added. The last modification will for brevity be referred to in the following text simply as "immersed percolation." It is believed to be the procedure generally followed in the leather laboratories.

In comparing these three modifications, namely, siphoning, percolation, and immersed percolation, all extractions were made with the same apparatus. Two series of extractions were made; in one series, siphoning was compared simultaneously with percolation and for the other series syphoning was compared at the same time with immersed percolation. This being done to eliminate as much as practicable all other variables. Table IV contains the data thus obtained.

While the individual results are not significant, the differences between the averages probably are, and they show that percolation gives slightly higher results (average 0.4 per cent.) than does siphoning, which in turn gives somewhat higher figures (average 0.9 per cent.) than does "immersed percolation."

Completeness of Extraction.

The official method is certainly a convenient one so far as amount of sample, temperature and time of extractions, and volume of extract are involved but the available data given in the committee reports previously cited show that this procedure does not remove all of what is termed "water soluble matter." It has also been stated frequently that some material continues to be removed indefinitely so that there is no precise end-point to the extraction. Some additional evidence is given in Table V along this line showing more particularly the effect of longer extraction under conditions of the present method. Continuous extractions for 7½ hours, collecting a liter of extract every 1½ hours, were made.

The results indicate that of the total extracted in 7½ hours: from 85 per cent. to 90 per cent. is removed in 3 hours; from 92.2 per cent. to 94.1 per cent. in 4½ hours; and from 96.7 per

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TABLE V.—COMPLETENESS OF EXTRACTION.

L. & P. No.	Description	Preparation	Per cent. water solubles					Per cent. extracted in the time stated below based upon the total extracted in 7½ hours				
			1st liter	2nd liter	3rd liter	4th liter	5th liter	1½ hours	3 hours	4½ hours	6 hours	7½ hours
34333	Oak	Shredded	21.1	3.2	1.8	1.3	0.9	74.6	86.0	92.2	96.7	100.0
34528	Texas bloom	"	23.2	3.0	1.6	1.2	0.9	77.6	87.6	93.0	97.0	100.0
34543	Union	"	22.0	2.5	1.3	0.9	0.7	80.3	89.4	94.1	97.4	100.0
34561	Oak	"	18.2	2.8	1.6	1.1	0.8	74.3	85.7	92.2	96.7	100.0
34585	Union	"	19.4	3.1	1.5	1.1	0.8	74.9	86.9	92.7	96.9	100.0
34588	Hemlock	"	22.4	2.4	1.2	1.0	0.8	80.6	89.2	93.5	97.1	100.0
34591	Hemlock	"	25.8	2.8	1.5	1.3	0.9	79.9	88.6	93.2	97.2	100.0

cent. to 97.4 per cent. in 6 hours. In other words, for the leathers used, the extraction was not sufficiently complete. It is believed that this is the greatest weakness of the present method making it extremely difficult to secure satisfactory concordance between different analysts.

Summary.

Data have been obtained which indicate that:

(1) Soaking over night is unnecessary;

(2) Between the range given in the experiments, the water solubles are increased on the average 0.9 per cent. for 5° C. rise in temperature;

(3) Variations in the flow during the extraction have little effect provided that finally the required volume of extract is collected in the specified time;

(4) Percolation tends to give slightly higher results than siphoning which in turn gives slightly higher figures than does "immersed percolation."

(5) Extraction by the official method is not sufficiently complete since of the total amount extracted in 7½ hours only from 85 per cent. to 90 per cent. was extracted in the specified 3 hours.

It is felt that the official method for determining water solubles in leather should at least be described more in detail so as to standardize both the procedure and apparatus as much as is necessary to eliminate the possible summation of small errors and should preferably be revised so as to give a more thorough extraction, bearing in mind, however, the desirability of keeping the time of extraction, the manipulation, and the necessary apparatus within reasonable and practicable limits.

Leather & Paper Laboratory,
Bureau of Chemistry,
Department of Agriculture, Washington, D. C.

Discussion.

F. P. Veitch: Mr. President, I had hoped that some discussion would arise on this very important subject of extracting leathers and extracting tanning materials, because I think really

the two are parts of one big problem. Unquestionably the time is coming, if it is not already here, when there will be more attention given to the analysis of leather, both for practical purposes and for research purposes, and it seems to me that we have to get our methods in such shape that different analysts can get reasonably good results.

This doesn't apply any more to leather than it does to tanning materials, and probably some of you, certainly the older members, will remember my general attitude on this subject in the past has always been that our extraction isn't drastic enough in any case. We don't get all of what we can properly call water soluble materials with our present methods.

I haven't seen any evidence yet to indicate that the leather itself is broken up by a reasonable length of time of extraction at as high as 55 or 60° for say 10, 12, or 15 hours. There is no nitrogen coming through; there is no evidence of any hide substance or material of that character in the extract, so I feel that one of the things that will contribute to getting concordant, and therefore, more accurate results, is going to be the elimination, as Mr. Frey said, of these little variations which all of us make in our work.

We have had some striking results along this line. The Forest Service has done a very nice piece of work on the recovery of paper mill bark. In that work, one of the things that has come out is the surprisingly different results on water solubles and extracted tannin. There were differences of 5 per cent. on water solubles, and 2 to 3 per cent. on tannin. Now, apparently those results were arrived at because of the different methods used. One analyst used a very small amount of bark; we used an amount which was supposed to give approximately our 4 grams of tannin in 100 cc.; the results were widely different. The rate of extraction on the barks apparently isn't a very important matter, whether we extract at the rate of 350 cc. in 1½ hours, or 500 cc. That wasn't as important as the amount of sample taken, and yet unquestionably it does play a part.

I feel that the Association should go over its methods of extraction, and polish them up, make them more elaborate, and more detailed, more definitely controlled, because we are not going to get satisfactory results unless we do.

L. M. WHITMORE: We analyzed four different leathers at temperatures ranging from 15° to 70° and we found that the increase in water solubles for 5° was just about 1 per cent. Three of the leathers—they were all big, composite samples, gave a fairly regular curve of increasing water solubles, but the fourth leather gave a very slight amount of increase until it got up to about 45°, and then there was a large increase in water solubles from there up to 70. We analyzed some original material and later analyzed the worn soles. We found that the degree of tannage in the worn soles was approximately the same as in the original leather. That seems to show that the 50° extraction is at least high enough, as everything that stayed in there at 50° under the original extraction was still in there when the soles were worn out.

THE EXTRACTION OF GREASE AND OIL FROM LEATHER.*

Discussion of Committee Report at the Atlantic City Meeting, May, 1919.

J. A. WILSON: There seems no need to review the principles employed in this work, since you have all had plenty of time to study the report. The Committee has recommended that chloroform replace petrol as the official solvent for extracting grease and oil from leather, considering such points as cost, inflammability, etc., entirely subordinate to the question of relative efficiency in extracting greases and oils from leather. Since the publication of the report, complaint has been made to me that for leathers containing only such oils and greases as are completely soluble in petrol, it would be extravagant to use a more expensive solvent.

Now, if an analyst knows that he will get the same result with petrol as with chloroform, I see no reason why he should not use petrol, even if chloroform were adopted as the official solvent, but the burden of proof that one solvent is as good as the other should rest with the analyst using the unofficial one.

The higher cost of chloroform will hardly enter into the calculations of those laboratories which recover the solvent after each extraction, but in any case, it will be more than offset by the change to a non-inflammable solvent. Some of the most careful

* See this JOURNAL 14, 140 (1919).

investigators have lost their lives through accidents in handling inflammable solvents, so the lessening of this danger ought to be welcomed by every laboratory.

PRESIDENT: Gentlemen, you have had the privilege of reading Mr. Wilson's report in the JOURNAL, and you have had time to study it, and to consider it. The matter is now before you for discussion, and we will be glad to hear from you.

DR. LOUIS E. LEVI: Gentlemen, you have read Mr. Wilson's report. The start that he has made in order to get a standard solvent for the extraction of fat is a very good one, and very commendable. The samples, as I understand, that Mr. Wilson and his collaborators had were all samples in the crust, that is, without any finishing or seasoning, in fact, without dyestuffs probably. In the selection of a solvent, one must take these things always into consideration, for we not only receive samples in the crust, but we receive finished samples at the same time.

Now, the question is: With these samples, will chloroform take out anything else from the leather besides the fat? We have been working at this for quite a long while, and we have gotten some very interesting results. The gentlemen here know that a tanner when finishing his stock is liable to use most anything to obtain the results desired.

I have a few figures here on the extraction of materials with chloroform and petrol ether, which is an excerpt from a paper which we intend to publish in the near future, and which will show very interesting results.

Light blood albumen is extracted by chloroform to the extent of 2.52 per cent., while petrol ether will only extract 1.66 per cent. Casein, the insoluble kind, is extracted by chloroform to the extent of 3.81 per cent., while petrol ether will extract only 0.85. We now come to a very interesting substance—that is shellac. Chloroform will extract 101.32 per cent. and three-fourths of the shellac at that was still in the extractor. Petrol ether will only extract 0.13 per cent. In shellac dissolved in weak ammonia and dried, chloroform will extract 18.30 per cent., while petrol ether will extract 1.41 per cent. Irish moss is extracted by chloroform to the extent of 0.25 per cent. and by petrol ether to the extent of 0.065 per cent. Gum tragacanth, chloroform

extracts 0.202 per cent. against petrol ether 0.023 per cent. Egg albumen, 0.201 per cent. extracted by chloroform as against 0.043 per cent. by petrol ether.

We also took up a few dyestuffs, and the ones I have here are only the synthetic aniline dyes, but we are working on osage orange, logwood and so forth. Logwood, you know, is quite often mixed, or rather, the direct blacks are often mixed with logwood—of course, in order to get the desired shade.

Alizerol brown, chloroform extracts 0.161, per cent., while petrol ether extracts 0.025 per cent. Direct black R is extracted by chloroform to the extent of 0.241 per cent. by petrol ether to the extent of 0.049 per cent. Acid green is extracted by chloroform to the extent of 0.094 per cent., against 0.023 per cent. by petrol ether. Bismark brown Y extra is extracted by chloroform to the amount of 0.188 per cent. against 0.029 per cent. by petrol ether; orange A, 0.312 per cent. by chloroform, against 0.069 per cent. by petrol ether.

We weighed an amount of waterless sod oil, placed it on wood pulp, then dried it on the steam bath for 48 hours, and extracted it 8 hours. The wood pulp was first extracted with chloroform and dried. That gave us 52.8 per cent. for chloroform, against 39.5 per cent. for petrol ether.

Now, we haven't completed this work, which we hope to do at some future date, and when it is finished, it will be very interesting. I would suggest that the Committee continue their very interesting work further, not only using chloroform, petrol ether, and so forth, but go after the synthetic solvents which are on the market to-day. I was going to say amyl acetate, but that is too high; let us go over to ethyl acetate, and if necessary, you can go to the benzol compounds, taking all of those solvents, and trying them out on all kinds of leather. I think that the gentlemen who started this interesting work will be able to make a report in the very near future, probably at the next meeting, and they will probably give us the ideal solvent which we have all been looking for.

DR. WILLIAM KLABER: May I ask if two-bath chrome leather was tested with these solvents? The point in question is that such leather contains quite a little sulphur, and this is extracted by almost every solvent I have ever tried, so that I have

never been able to get a determination of the fat that was in any way satisfactory.

J. A. WILSON: When analyzing leather containing sulphur, I prefer to extract the sulphur with the fat and then determine the amount of sulphur in the extract by oxidizing to sulphate and precipitating with barium chloride in the regular way.

DR. WILLIAM KLABER: I have tried oxidation but have never gotten satisfactory results.

J. A. WILSON: One method we have used for this is to digest the extract with a boiling solution of potassium dichromate and hydrochloric acid. The oxidation can also be effected by the peroxide fusion method.

PRESIDENT: Mr. Wilson, what were the samples you sent around; were they upper leathers?

J. A. WILSON: The samples included both light and heavy upper leathers, sole leather, and strap leather. The tannages were chrome, vegetable, and chrome-vegetable combination. All but three of the leathers were in an unfinished state, as Dr. Levi has pointed out. I infer from Dr. Levi's remarks that he would have preferred to see a larger proportion of the work devoted to finished leathers and the analysis of the extracted matters. However, had the Committee attempted to work that way, we should probably have failed to get any very definite results, because we have no satisfactory method for determining the proportion of non-fatty matter in the extract. On the other hand, I think we have proved by our indirect methods that chloroform does extract more fats, oils, and waxes from leather than petrol does. We know from qualitative tests that chloroform extracts traces of tannins and possibly other non-fatty matters from some leathers, but we believe any error from this source is insignificant compared to the error due to incomplete extraction when using petrol.

In considering the solvent action of chloroform upon substances apt to be contained in finished leathers that were not present in the unfinished leathers we used, it is well to calculate roughly what proportion they bear to the total weight of leather. For example, the amount of dyestuff present in the ordinary leather is so small that in many cases no very big error would be

introduced if all of the dye were extracted as fat; and we know that it isn't all extracted by any means. It should also be borne in mind that, if some of the organic constituents of the finish are not extracted with the fats, they will be calculated as fixed tannins, and it is doubtful that calling them fixed tannins is to be preferred to calling them fats.

Dr. C. G. Bumcke: I do not think that we can select one solvent for determining what you comprise here under the name of "fat." We know, that in oil and fat analysis, we make use of different solvents for the separation of different parts of oils or fats. For instance, we know that mineral oils, paraffine wax and most unaltered vegetable and animal oils and fats are soluble in petrol ether, while oxidized, polymerized or condensed fatty matter requires other solvents like alcohol, ethyl ether, benzol or chloroform.

Now, I think we will probably come to similar proceedings in the extraction of grease and oil from leather, first using petrol ether then follow with another solvent. We feel sure that what we get from an extraction with petrol ether is what we call "fat." As Dr. Levi and others pointed out the amount of other organic matter that dissolves in petrol ether is a rather negligible quantity. But, we do not extract all that we classify as fatty matter, for instance the oxidized fatty matter in moellons and sulphonated oils. We have to have another solvent for these, so for this reason I think, we will finally come to the use of at least two different solvents.

There is another thing which we have not taken into consideration, that is that, according to the quantity of oil present in the leather, the oil-petrol ether mixture becomes more or less a solvent for oxidized products and soaps. In oil analysis we meet this condition by using in the beginning a large excess of petrol ether in order to dilute this oily solution so much that it is no longer a solvent for soaps or oxidized fatty matter. But I do not see how we can overcome this condition in the ordinary extraction apparatus where the first extraction comes down in a rather concentrated solution. If it is desired to know the amount of oxidized fatty matter that went into the petrol ether solution, this should be diluted with petrol ether at least 1:50, settle over

night and then be filtered. After washing the flask and filter sufficiently with petrol ether, the oxidized fatty matter which mostly adheres to the wall of the flask may be taken up with alcohol or ethyl ether. The rest of the oxidized fatty matter still in the leather may then be extracted with ethyl ether or chloroform. Any amount of soap in the petrol ether as well as in the chloroform extract should be calculated from the ash determination.

DR. LOUIS E. LEVI: I think the qestion of using more than one solvent for the same sample is almost precluded. When you get a sample sent up to your laboratory, "We really would like to have the facts to-morrow morning early." Say the sample came up at about 4 o'clock in the afternoon; if we had to use more than one solvent, I hardly think we would get that analysis out by the next morning. That is a point that isn't taken into consideration.

F. P. VEITCH: Mr. President, I should just like to add here, with reference to some remarks made by Dr. Bumcke, that we didn't get all the paraffine, or petrolatum, or tallow, or moellon oil out with petrol ether, and that was in a long extraction of 24 hours, steady extraction. So that you see even petroleum ether cannot be relied upon to get all of what you might call, if you chose, fats. In every one of those cases, however, chloroform removed all of those materials.

DR. C. G. BUMCKE: Mr. Veitch has stated that he wasn't able to extract the full amount of mineral oils, paraffine, or lard oil with petrol ether. Now, I want to ask Mr. Veitch whether he has tried their solubility in petrol ether before he put them into the sand or leather? They might have contained some material, from the previous treatment. For instance, I have found ash in clear oils after the treatment with fullers' earth; mineral oils and lard oils often contain moisture. The oils that Mr. Veitch used probably contained soaps or moisture or tarry matter which would not re-appear in his petrol ether extract and thus lead to a wrong conclusion. Chloroform is more likely to take up soapy or tarry matter while petrol ether is not.

F. P. VEITCH: I don't recall definitely the details. Of course there is another thing. There might be some moisture in some of these that would account for the lower results.

EFFECT OF HARD WATER ON TANNIN—REPORT OF 1919 COMMITTEE.

By T. A. Faust, Chairman.

The Committee conducted no laboratory work this year as it was thought that the data obtained during the past 2 years was reliable, and that the work this year should be confined to making the proper deductions from this data, and to explain the analogy between our laboratory figures and practical results.

The Chairman wrote a letter to Mr. Wilson which was incorporated in Mr. Wilson's article[1] in the March number of the JOURNAL. The report of this Committee is a brief discussion of this letter and Mr. Wilson's reply.

Attention was called to the fact that 2 years laboratory work indicated no considerable destruction of tannin by the salts in hard water with the exception of calcium sulphate. It must be remembered that last year's laboratory work was carried out by making liquors according to tannery practice, and then testing these liquors. At no time in the Committee work did we use hard water for making analyses, as the proportion of tannin to salts in such a case, using water containing thirty parts per 100,000 temporary hardness, would be as 4 grams tannin is to 0.3 gram salts, where as in a 50° tannery liquor the proportions would be as four parts tannin is to two-hundreth part salts; or in other words only one-fifteenth as great.

However, the Committee definitely established the fact that in laboratory work using the hide-powder method there is no considerable destruction of tannin, although practical experience in two tanneries showed definitely a considerable saving of tannin when using soft water.

It is therefore, evident that some factor enters into practical working conditions which is not evident in the laboratory work.

It is quite true that the hide-powder method has its limitations in such investigations and Wilson and Kern definitely proved that solutions of calcium sulphate analyzed by the hide-powder method actually showed a percentage of tannin. This would, therefore, raise the tannin figure and compensate for any reduction in tannin caused by the precipitation of tannin with lime

[1] This JOURNAL 14, 93 (1919).

or magnesia. This is a possible explanation of the reason the committee could prove no considerable loss of tan.

However, tannery practice shows a very marked difference between hard water and soft water; hard water gives turbid and dull liquors whereas soft water gives clear liquors and gives better sappage due to the fact that the tannin is much more active. No doubt this difference in the efficiency of the tannin is due to some extent to the degree of clarity of the liquor but it is also evident that the presence of hide has some influence on this phenomena due to the interference of these salts with the tanning action.

The Chairman is reticent about going into the theory of tanning but in his letter to Mr. Wilson made the following statement:

"It is quite possible that the salts (those producing hardness in water) are ionized forming a gelatine salt such as Dr. Procter describes in a recent article. If we accept your theory of an electrical neutralization, this gelatine salt, being a combination of the positive electro charge of the gel and the negatve charge of the acid ion, would reduce the natural electro-chemical attraction between the proteid matter and the tannin. In other words the liberated base of the hard water salts would attract a part of the negative potentials of the tannin, whereas with soft water there would be no diminution of the negative charge."

Mr. Wilson in his article contests the physical combination theory and explains the Procter-Wilson theory, stating that it can be considered either an electrical or chemical precipitation. Assuming this theory we can agree with his statement that the presence of an electrolyte in a tan liquor will lower the difference of potential between the gel and the tan molecules, and it would, as Mr. Wilson states, lessen the astringency and stability of the tannin.

However, it appears that the explanation of the results of this Committee will depend entirely on the theory of tannage itself, and as this theory has not been conclusively established it is believed that the reason for the results noticed in practice; namely, the apparent destruction of tannin by hard water must be left in abeyance until such time that we have more light on this theory.

EXTRACTION OF LEATHER STUFFING OILS AND GREASES FROM SAND.*

By F. P. Veitch and M. G. Hunt.

Wilson and Kern (This JOURNAL 13, 138-41), have redirected attention to the well known fact that the solubility of oils, greases and their alteration products varies in different solvents. The report of the A. L. C. A. Committee on the extraction of grease and oil from leather (This JOURNAL 14, 140-78), confirms Wilson and Kern's work, but neither the experiments there reported nor those of Wilson and Kern were so planned as to show the proportion of oil, grease and alteration products actually in the leather, which was extracted by each of the solvents employed. Furthermore, it is known that several of the solvents extracted from the leather materials other than oils, greases and their alteration products, and thus the problem of the proper solvent for the determination of oils and greases in leather is left unsolved.

This laboratory in conducting extended experiments on the effects of greases on leathers found it necessary to consider the changes which take place in the greases applied to the leathers, to use solvents which will throw some light on this question, as well as secure additional information on the complete extraction of the grease.

In order that the oil and grease content and the alteration of the oils and grease might be known with approximate accuracy, it was decided to mix the oils and greases with a substance which would have no direct chemical action on them.

White crushed quartz (30 to 40 mesh) was chosen as it has several advantages. The individual grains do not absorb the oils and greases which are held mechanically on the surface, the sand is inactive to oils and greases, and is not attacked by the organic solvents.

Eighteen commercial oils and greases, representative of those used in stuffing leathers, and of drying, semi-drying, and non-drying oils were used.

Ethyl ether, chloroform, and petroleum ether (B. P. 35° C. to 55° C.) were chosen as the solvents for these experiments as

*Read at the Atlantic City Meeting of the A. L. C. A., May 22, 1919.

they all have a relatively low boiling point which is advantageous in that the solvent can be readily removed from the extracted oils and the low temperature of extraction is not so liable to start decomposition of the oils and greases or of the leather. The solubility of sulphur, which is present in some leathers, in carbon disulphide and the relatively high boiling point of carbon tetrachloride were considered sufficient reasons for eliminating them as practical solvents.

Manner of Conducting Experiments.

The sand was washed by decantation with distilled water and petroleum ether to remove dirt and any adhering oil or grease and then dried to constant weight at 100° C. Approximately 30-gram samples were weighed out into tannin dishes equipped with a short stirring rod and enough oil in each case added to make a good paste after well mixing, but not enough excess to flow off on standing. The greases were melted and thoroughly stirred in while still liquid. The dishes were then set aside in a covered desiccator with a side aperture open to the air and stirred once each day. After the first week they were weighed twice a week until approximately constant weight was obtained, which required a little over 3 weeks. Small portions were then removed, taking care to get as representative a sample as possible, and a portion extracted with one of the three solvents. The extractions were made in a Johnson extractor for 24 hours and in all cases the extract was heated 2 hours on the steam bath and then 2 hours in an oven at 100° C. to remove the solvent and all moisture. A preliminary extraction was made for 12, 24 and 36 hours and it was found that there was a slight increase in weight up to the 24-hour period but on further extraction no increase in weight was obtained. Likewise it was found that 2 hours on the steam bath and 2 hours heating at 100° C. was necessary to remove petroleum ether so that the same time was allowed for the removal of the other two solvents. Attention may be called to the known fact that drying the extracted oils and greases under atmospheric conditions may lead to erroneous results from oxidation changes in the oil during drying, especially with drying and semi-drying oils. It is believed, however, (and the figures in the tables confirm the opinion) that since the samples had been exposed to the

air from 4 to 8 weeks previous to extraction, that oxidation was practically complete and the error on drying in air at 100° C. for 4 hours is negligible.

A month later the dishes were carefully weighed and samples taken therefrom were extracted with chloroform and ethyl ether respectively.

In all cases, the quantity of oil or grease present at the time of extraction was calculated from the weight of the dish and its contents, thus correcting for any addition of oxygen and loss of moisture or volatile matter which had been present in the original oils and greases. Some difficulty was experienced in getting a thoroughly representative sample due to the hardening of the oils on account of oxidation. For this reason differences of ½ per cent. or less are considered insignificant.

Table I shows the quantities extracted as compared with the quantities originally added. The results are more easily visualized in the diagram. It must be borne in mind on examining the diagram that the connecting lines do not represent any definite curve as the arrangement of the oils and greases was arbitrarily chosen on the basis of the quantity of oil added. The connecting lines are simply to assist in visualizing and making the comparisons more striking.

It will be seen that petroleum ether has extracted 90 per cent. or more of rosin oil, wool grease, stearine, tallow, lard oil, petrolatum, and amorphous wax; between 75 and 90 per cent. of whale oil and paraffine oil; between 50 and 75 per cent. of red oil, cod oil, and sulphonated neatsfoot; between 25 and 50 per cent. of cotton-seed oil and sulphonated cod oil; 22 per cent. of corn oil, and only 8 per cent. of the linseed oil present.

Chloroform extracts less than 90 per cent. only in the case of linseed oil of which 80 per cent. is extracted.

Ethyl ether extracts less than 90 per cent. only in the cases of linseed oil where 60 per cent. is extracted, sulphonated neatsfoot where 86 per cent. is extracted and sulphonated cod oil where 73 per cent. is extracted.

With chloroform, extraction is practically complete in the case of menhaden and cod oils, wool grease, arctic dubbing, stearine,

TABLE I.—EXTRACTION OF GREASES FROM SAND AND GREASE MIXTURES.

Grease	L.& P. No.	Grease added %	Grease present 10 days %	Grease present 14 days %	Grease present 18 days %	Petroleum ether data: Grease present when extracted 23 days %	Petroleum ether data: Grease present when extracted 71 days %	Petroleum ether data: Extract after 23 days %	Petroleum ether data: Extract after 71 days %	Chloroform data: Grease present when extracted 39 days %	Chloroform data: Grease present when extracted 59 days %	Chloroform data: Extract after 39 days %	Chloroform data: Extract after 59 days %	Ethyl ether data: Grease present when extracted 57 days %	Ethyl ether data: Extract after 57 days %
Linseed oil	33574	12.0	13.3	13.3	13.3	13.3	13.3	0.9	1.0	13.3	13.3	11.6	10.4	13.3	6.7
Corn oil	35482	12.0	12.8	13.0	13.0	13.0	12.8	3.5	2.9	12.9	12.8	12.1	11.9	12.8	11.1
Cotton-seed oil	35481	16.4	17.1	17.5	17.7	17.8	17.4	7.8	6.5	17.7	17.5	16.5	16.4	17.5	15.8
Menhaden oil	35098	16.8	20.2	20.4	20.5	20.6	20.4	8.8	7.7	20.6	20.4	19.0	20.4	20.6	19.0
Sulphonated cod oil	34441	15.2	14.7	14.6	14.6	14.6	14.7	8.7	7.2	14.6	14.7	13.4	13.2	14.7	10.9
Red oil	35113	9.4	9.9	9.9	10.0	10.0	10.1	6.8	6.1	10.2	10.2	9.4	9.6	10.2	8.9
Cod oil	35121	12.3	13.4	13.4	13.4	13.4	13.4	12.1	8.9	13.4	13.4	12.2	12.4	13.4	11.8
Sulphonated neatsfoot oil	34442	14.8	11.9	11.9	11.9	11.9	13.1	10.0	7.8	12.0	13.1	10.8	11.2	12.0	10.4
Waterless moellon	35272	13.9	13.9	13.9	13.9	14.0	14.1	12.0	9.3	14.0	14.1	13.8	13.5	14.1	12.9
Paraffin oil	35174	13.5	13.5	13.5	13.5	13.6	13.7	11.7	11.4	13.7	13.7	12.6	13.7	13.7	12.2
Tallow	35123	11.8	10.6	10.6	10.6	10.7	10.7	9.5	9.3	10.7	10.7	11.0	11.2	10.7	10.4
Whale oil	35529	10.9	11.8	11.8	11.8	11.8	11.9	10.3—	9.1	11.8	11.8	10.8	11.5	11.8	10.3
Third run rosin oil	22918	14.0	13.8	14.0	14.3	14.6	15.1	12.3	13.4	15.0	15.1	14.2	14.3	15.1	13.0
Wool grease	35269	11.0	11.0	11.0	11.1	11.1	11.3	8.0	10.1	11.2	11.3	11.1	10.9	11.2	10.5
Amorphous wax	34972	11.4	11.4	11.4	11.4	11.5	11.5	10.9	10.6	11.5	11.5	11.2	11.1	11.5	11.0
Petrolatum	35104	14.4	14.4	14.4	14.4	14.4	14.5	13.8	13.4	14.5	14.5	13.9	14.0	14.5	13.7
Lard oil (winter strain)	35117	16.8	17.1	17.1	17.2	17.2	17.4	14.8	16.6	17.4	17.4	17.3	17.6	17.4	17.0
Stearine	35122	11.4	11.5	11.5	11.5	11.5	11.5	11.8	11.3	11.5	11.5	11.2	11.3	11.5	11.4

tallow, lard oil, paraffine, petrolatum, and amorphous wax. Only in the case of corn oil, linseed oil, cod oil, sulphonated neatsfoot, and sulphonated cod oil is less than 95 per cent. extracted.

To get a comparison of the amounts of oil and greases, or other leather components extracted from leather, three representative samples (one upper and two sole leathers with a relative high and low water soluble) were chosen and extracted in the same way as the sand with both chloroform and petroleum ether. Table II shows that in all cases the chloroform gave the highest percentages as would be assumed from the results obtained in the extraction of the sand. It will be noted that the sole leather with the highest water soluble gave the smallest difference between the amount extracted by the two solvents, which would seem to indicate that no water soluble is included in the chloroform extract.

From these results it would appear that petroleum ether has by far the lowest solvent action of any of the three, only petrolatum being as soluble as in chloroform. In every case chloroform is as good as or better than ethyl ether, although the latter appears as good for the greases used but not for the oils. In no case is petroleum ether better than ethyl ether. Upon longer standing the fish oils appear to become less soluble in petroleum ether and slightly more soluble in chloroform although no further oxidation is shown by the weight. From these results it would appear that although chloroform is not 100 per cent. efficient it is by far the best solvent for oils and greases in general, and, the solubilities of other leather substances being eliminated or standardized, it would give more concordant and better results than either of the other two solvents.

TABLE II—COMPARISON BETWEEN PETROLIC ETHER AND CHLOROFORM FOR EXTRACTING GREASE FROM LEATHER.

L. & P. No.	Description	Petroleum ether extract Per cent.	Chloroform extract Per cent.	Moisture Per cent.	Water soluble Per cent.
35766	Chrome retan upper	15.8	17.0	6.4	—
34529	Sawed oak tan sole	2.9	3.6	7.6	27.2
34579	Scoured oak tan sole	2.0	3.1	8.7	15.4

SULPHITE CELLULOSE IN SYNTHETIC TANS, TANNING EXTRACTS AND IN LEATHER.

1919 COMMITTEE REPORT.

By C. M. Kernahan, Chairman.

As the Procter-Hirst test was found to be unsatisfactory, or rather did not differentiate between the presence of sulphite-cellulose and synthetic tannin, the writer was appointed Chairman of a committee to make further investigations as to making a separation of these two materials. I must admit that I have been unable to make the investigations which I desired to make on this matter, owing to pressure of other work.

The only report which I have to make is the work of Mr. Hayes and myself; the other collaborators having stated that they did not have time to get their reports in.

The samples which I sent out, were as follows:

Sample No. 1—containing 20 per cent synthetic tannin and 80 per cent. treated quebracho extract.

Sample No. 2—containing 20 per cent. sulphite cellulose and 80 per cent. treated quebracho extract.

Sample No. 3—containing 10 per cent. synthetic tannin, 10 per cent. sulphite cellulose and 80 per cent. treated quebracho extract.

The methods suggested to differentiate between sulphite cellulose and synthetic tannin, are those of W. Appelius and Rudolf Schmidt, and are as follows:

1. *Preparation of Cinchonine Solution*:

Mix in a graduated liter flask, 5 grams of cinchonine with 100 cc. of water, and add, drop by drop, concentrated sulphuric acid until a clear solution is obtained. Fill up to mark, and shake well.

2. *Test*:

One hundred cubic centimeters tannin solution of analytical strength (filtration unnecessary) is boiled a short time with 5 cc., 25 per cent. hydrochloric acid. The solution is then cooled and filtered if not clear. Fifty cubic centimeters of the clear filtrate is placed in an Erlenmeyer flask, and 20 cc. of above cinchonine solution is added without shaking. If a precipitate forms, it is either from (*a*) a catechol tannin, or (*b*) sulphite cellulose.

If no sulphite cellulose is present, the precipitate will be redissolved on heating the mixture to the boiling point, without shaking. If the grayish-white precipitate due to sulphite cellulose is formed, it will be quite bulky and form a blackish-brown lumpy mass.

Differentiation of Synthetic Tannin and Sulphite Cellulose.

Preparation of Diazo Solution:

Five grams para-nitraniline are placed in a graduated 500 cc. flask with 25 cc. water and 6 cc. concentrated sulphuric acid. Shake well and add 100 cc. water and 3 grams sodium nitrate in 25 cc. water. Fill up to the mark and do not expose to light.

Test:

Fifty cubic centimeters tannin solution and 15 cc. of above solution are mixed, and if not clear, filter. Add excess of sodium hydrate to the filtrate. In the presence of synthetic tannin, the solution will be colored blood red. In examining aqueous extracts from leather and other solutions containing only small quantities of synthetic tannin, it is advisable to pour the solution (*i. e.*, the mixture of tannin solution and diazo solution) on to filter paper and, after drying, to place a drop of sodium hydrate on the paper. According to the quantity of synthetic tannin present, a red-rimmed or dark brown spot will become visible.

Mr. Hayes reported as follows:

Test for Sulphite Cellulose by Addition of Cinchonine Solution

Tests	Sample No. 1	Sample No. 2	Sample No. 3
Addition of reagent gave....	Ppt.	Ppt.	Ppt.
Heating gave...............	Residue	Residue	Residue

The results which I obtained were as follows:

Tests	Sample No. 1	Sample No. 2	Sample No. 3
Addition of reagent gave....	Ppt.	Ppt.	Ppt.
Heating gave...............	Residue	Residue	Residue

On the method to differentiate between sulphite cellulose and synthetic tannin, Mr. Hayes reported as follows:

"Extract No. 1 gave a distinctly deeper color. By diluting the tannin solution (2 - 10), the distinction in color became more marked."

It is assumed from this, that all three samples gave the blood red color, but that sample No. 1, containing the highest percentage of synthetic tannin, gave a coloration which may be distinguished from samples No. 2 and No. 3, containing various amounts of sulphite cellulose and synthetic tannin.

The writer has experimented along these lines, using various amounts (from 5 - 20 per cent.) of synthetic tannin and has noted by the use of this test, that it is practically impossible to make any distinction as to the coloration produced by the addition of the diazo solution to the several tannin solutions, between those containing sulphite cellulose and those containing synthetic tannin, except in the case where the sample contained 20 per cent. of synthetic tannin. In samples containing less than 20 per cent. it was very difficult to make any positive distinction; the distinction becoming more difficult as the percentage of synthetic tannin was decreased.

Mr. Hayes comments on the cinchonine method, as follows:

"There was nothing characteristic or distinctive about the behavior of any of the extracts, other than that extract No. 1 gave a heavier residue than extracts No. 2 and No. 3, and a less clear supernatant liquor."

On the method by the use of the Diazo solution, he comments as follows:

"Although the difference in color was distinctive, criticism on the value of the test must necessarily be withheld, as the strength of synthetic tannin present in the test extract was unknown."

It will be noted that by the use of cinchonine, sample No. 1 containing no sulphite cellulose, showed a precipitate, and as Mr. Small reports, a heavier precipitate than samples No. 2 and No. 3, which did contain sulphite cellulose. This eliminates this method as a means of distinguishing between these two materials.

The method by the use of the Diazo solution, does make a distinction to a certain extent, but the Chairman believes that in admixtures containing small amounts of synthetic tannin and sulphite cellulose, it becomes very difficult to make any differentiation. It is my belief that in samples which show a precipitation by either the Procter-Hirst test or the cinchonine test, an approximation or at least conclusions can be drawn as to whether

sulphite cellulose or synthetic tannin is present, by the reading of the regular tannin analysis.

Sulphite cellulose, with its comparatively low purity and high non-tannins, would greatly increase the non-tannins of the resulting admixture, whereas synthetic tannin, with its high purity and comparatively low non-tannins, would not increase the non-tannins, and in that way, some conclusions could be drawn as to whether the mixture contained synthetic tannin or sulphite cellulose, provided always that the Procter-Hirst test indicated either.

The statement as to the purity of synthetic tannin, is based upon the analysis of the synthetic tannin which was used in this Committee work. It is quite possible that the synthetic tannin which was used to some extent in this country before the war, and which was the European product, did not show any such high degree of purity.

It seems apparent, from the work of Yocum and Nelson, and the data herein contained, that the Procter-Hirst test resolves itself into a test for SO_3 radicle, combined with organic base.

SULPHONATED OILS.*

By Dr. C. G. Bumcke.

It was only when I received the program of our present meeting that I learned that I was going to say something about sulphonated oils to-day. Whoever was guilty of putting my name on the program, I have to thank for his or their confidence trusting that I could tell you something about sulphonated oils even without preparation. Indeed I had no time to prepare an elaborate treatise for you but I am willing to tell you something of my recent experience concerning the interpretation of the analysis of sulphonated oils and its relation to their action on leather.

I am under the impression that the majority of us are not in a position to give a right interpretation of the different figures of the analysis of a sulphonated oil as to their respective value and effect on the softness of the leather, grain, color, etc. All these things should be investigated under close observation of all pre-

*Read at the Annual Meeting of the A. L. C. A. May 23, 1919.

vailing conditions and with a complete analysis of the oil on hand.

I have not forgotten the remark made here, by one of our members when we were discussing which determinations we should incorporate in our official method for testing sulphonated oils. He remarked: "What's the use to determine all those figures?" He was perfectly right, there is no use to obtain the analytical data if we can get along without them by trying the oil for a certain purpose and then from failure or success make a deduction as to the usefulness of the oil. But if we want to progress and avoid failure we must not only make a full analysis but also must be in a position to explain the effect of the different items of the analysis. Unfortunately enough, we are not yet in a position to do that, we have hardly made a beginning, most of our knowledge in this line is based more on theory and conjecture than on analytical data. I think this is the place where we should exchange our experiences in this line and so I will make a beginning.

If a chemist is called upon to decide whether a certain sulphonated oil is fit to be used in a certain process, if he is very careful, he will determine the content of water, total fatty matter, combined SO_3, unsaponifiable and perhaps ammonia or ash and probably make a few preliminary tests and then say the oil is fit or not fit, but he could hardly tell the reason why he calls one fit and the other not fit. Still more difficulties are encountered if he had to select the best among a number of oils that he would consider fit, and even more than his decision, will count the matter of price. But I am not here to talk prices but sulphonated oils, and so I will tell you how I found out from analytical figures, why one sulphonated oil stripped colors and another did not.

As is usually the case, it was made as hard for me as possible as every tanner is suspicious of a chemist because in ninety-nine cases out of one hundred he fears that the chemist might carry all his secrets away. The only facts submitted to me were the analyses of the tanner's chemist, two samples of sulphonated cod oil supposed to be type samples of the good and bad oil and a good and bad piece of leather. A small sample of the dye was not submitted and could not be obtained. Now the two analyses made by the tanner's chemist gave the following figures:

	A. Satisfactory oil		B. Unsatisfactory oil	
	No. 1 Per cent.	Calculated for dry oil	No. 2 Per cent.	Calculated for dry oil
Moisture	24.85	—	26.25	—
Total fatty matter	72.08	95.92	69.03	93.58
Total SO_3	3.27	4.35	2.64	3.58
	100.20	100.27	97.92	97.16
SO_3 in salts	0.37	0.49	0.28	0.38
Combined SO_3	2.90	3.86	2.36	3.20
Unsaponifiable	0.13	0.17	0.20	0.27
Ash	2.94	3.91	4.50	6.10
Acid value	58.50	77.85	23.58	31.98
Calculated as oleic acid	29.25	38.92	11.79	15.99

His remarks were: The bad effects of oil B in fat liquoring is due to the following reasons:

1. The degree of sulphonation is too low as is shown by the SO_3 content, acid value and appearance (color) of the oil.

2. The ash contains a considerable amount of sodium salts which give an alkaline reaction and may exert a stripping action on the color.

3. Our lake water contains a considerable amount of hardness which in turn combines with the free fatty acids, due to insufficient sulphonation, in the oil, and soap material (curdy precipitate) is produced; the latter acts as a stripping agent and causes spots on the colored leather."

To this I made the following comments:

1. The degree of sulphonation can only be judged from the content of combined SO_3, the acid value and the color of the oil have nothing to do with it, as both may vary considerably in the original oils. The combined SO_3 in oil A is about ½ per cent. higher than in oil B.

2. The ash of both oils is naturally almost nothing but sodium salts (mostly Na_2SO_4 with some Na_2CO_3). Sodium carbonate always forms, when soap is burnt, or organic matter (oil) in the presence of alkali. Free alkali cannot be in the sulphonated oil when free fatty acids are present. The stripping effect of the one oil can, therefore, only be traced to the higher amount of soap and not to the alkalinity of the ash which is only developed through the burning of the oil.

3. The lime, etc., in the lake water will not react very readily with free fatty acids in cold or lukewarm water while lime, magnesia and iron salts act very quickly on soaps that dissolve easily in the same medium (water). The soaps of lime, magnesia, iron, etc., being insoluble in water cannot very well have an effect on the stripping of the colors though they may cause spots on leather. The only remedy for this would be a softening of the water before it is used for making a fat liquor and for washing the leather as well. Hardness in water as we all know, is rather undesirable for leather making.

You see I did not quite agree with his interpretation and as his analyses were not complete enough to make the right deductions, I went to work and analyzed the samples submitted which were supposed to be identical with those tested by him. I found the following figures:

No. 3 Oil A.

This lot works satisfactorily and does not strip the color.

After settling at room temperature the oil is fairly clear, it shows a white precipitate and water at the bottom. No pressure developed in the bottle. It emulsifies immediately in water making a white emulsion which with a few drops of ammonia gives an opaque solution.

The sample was well shaken before testing.

	Per cent.		Per cent.
Water	25.13	SO_3 in salts	0.417
Total fatty matter	70.14	Combined SO_3	1.946
Total SO_3	2.363	Sulpho. fatty acid	9.24
NaO_2	1.285	Neutral oil	23.95
NH_3	0.111	Ash	3.05
	——	1.285 Na_2O =	2.94 Na_2SO_4
	99.029		

0.417 SO_3 in salts = 0.740 Na_2SO_4 = 0.323 Na_2O

1.946 combined SO_3 need for neutralization 0.757 "

1.080 "

Present 1.285 "

1.98 fatty acids (M = 300) combine with 0.205 "

1.96 " " " " " 0.111 NH_3

3.94 " " are present as soap.

	Per cent.
Total fatty matter	70.14
Neutral oil	23.95
Fatty acids	46.19
Fatty acids in soap	3.94
Free fatty acids	42.25

Found by Titration: Acid value 74.7 corresponding to 37.54 per cent. oleic acid. On account of the presence of ammonia the titration cannot be quite correct. The amount of fatty acid combined with ammonia should be deducted 37.54- 1.80 = 35.74 per cent.

	Per cent.
For M = 300, the acid value 74.7 =	39.94 fatty acid
	1.96 fatty acid in ammonia soap
	37.98 free fatty acids

No. 4 Oil B.

This lot is said to give trouble when applied to their hides, especially to strip the colors.

The oil after settling at room temperature is fairly clear. It shows a dark gray precipitate and little water at the bottom. A gas of bad odor (H_2S) developed pressure in the bottle. It forms clear threads when poured into water which dissolve slowly by shaking to an opaque solution. This gets perfectly clear by the addition of a few drops of ammonia.

The sample was well shaken before testing.

	Per cent.		Per cent.
Water	29.45	SO_3 in salts	0.851
Total fatty matter	65.31	Combined SO_3	1.913
Total SO_3	2.764	Sulpho. fatty acid	9.09
Na_2O	1.920	Neutral oils	28.03
NH_3	0.063	Ash	4.46
		1.92 Na_2O =	4.40 Na_2SO_4
	99.507		

0.851 SO_3 in salts = 1.510 Na_2SO_4 =	0.659 Na_2O
1.913 combined SO_3 need for neutralization	0.741 "
	1.400 "
Total Na_2O present	1.920 "
5.03 fatty acids (M = 300) combine with	0.520 "
1.11 " " " " "	0.063 ammonia
6.14 fatty acids present in soaps.	

	Per cent.
Total fatty matter	65.31
Neutral oil	28.03
Fatty acids	37.28
Fatty acids in soaps	6.14
Free fatty acids	31.14

Found by titration:

	Per cent.
Acid value	51.2
Calculated as oleic acid	25.73
Or as fatty acid with M = 300	27.39
From which the amount of fatty acid in ammonia soap must be deducted	1.11
Free fatty acids	26.28

As the amount of water shows a difference of more than 4 per cent. it is more correct to compare the two oils when their figures are calculated for the product free from water.

	Oil A		Oil B	
	No. 3 Original oil	No. 5 Calculated for dry oil	No. 1 Original oil	No. 6 Calculated for dry oil
Total fatty matter	70.14	93.68	65.31	92.57
Total SO_3	2.363	3.157	2.764	3.919
Total Na_2O	1.285	1.717	1.920	2.722
NH_3	0.111	0.148	0.063	0.089
Glycerine and imp. and loss	0.971	1.298	0.493	0.700
	74.870	100.000	70.550	100.000
Water	25.13		29.45	
	100.00		100.00	
SO_3 in salts	0.417	0.557	0.851	1.206
Comb. SO_3	1.946	2.599	1.913	2.712
Sulpho. fatty acid	9.24	12.34	9.09	12.88
Neutral oil	23.95	31.99	28.03	39.73
Ash	3.05	4.07	4.46	6.32
Above amount of Na_2O = Na_2SO_4	2.94	—	4.40	—
Fatty acids in soap	3.94	5.26	6.14	8.70
Free fatty acids (by difference)	42.25	56.43	31.14	44.14
Acid value =	74.7	99.7	51.2	72.57
Free fatty acid as oleic acid (by titration)	37.57	50.18	25.73	36.48
For fatty acid (M = 300) minus fatty acid combined with ammonia	37.98	50.72	27.39	38.81

2.363 SO_3 = 4.192 Na_2SO_4 2.764 SO_3 = 4.906 Na_2SO_4

There could hardly be any carbonate in the ash as sufficient sulphuric acid is present to transform all sodium oxide into sodium sulphate.

The only figures that agree with analyses No. 1 and No. 2 are those of the ash test and the water test of No. 3, all the other tests vary so much that the samples tested in the tannery could not have been identical with those submitted to me. The acid value of No. 1 is greater than that of No. 2, so is that of No. 3 greater than that of No. 4 but the figures of No. 3 and No. 4 are far off from those of No. 1 and No. 2.

With the report of my analyses I made the following remarks:

The biggest difference in the two oils is best seen by their behavior in water. The one marked lot A dissolves easily to a white emulsion while the lot B dissolves only slowly forming an opaque solution. The explanation for this is given in the analysis which shows for the lot B more sodium oxide and consequently more soap and less free fatty acids than the lot A.

The degree of sulphonation does not show much difference for the two oils. The original analysis makes it appear a little better for the *lot A,* while in proportion to the total fatty matter the amount of sulpho. fatty acids or the combined SO_3 is slightly higher in the *lot B* as is indicated by the figures when calculated for the dry (anhydrous) product.

The only reason for the stripping of the colors appears to be the presence of the greater amount of soap and the lower percentage of free acids in the lot B.

Each oil is good in its proper place, the one (A) serves as acid fat liquor immediately, it only needs some mixing with water while the other (B) will only give an emulsion after previously being mixed with some saponifiable (animal or vegetable) or some mineral oil.

As we learn usually more from failure than if everything goes smoothly, I will give you another analysis of an oil that did not work satisfactorily. I may mention by the way that the party during the embargo last year could not get the oil they were used to and used this oil in the meantime but with unsatisfactory results. It seemed to me very interesting to find out why this oil, that otherwise had a fairly good appearance, did not give satisfaction.

The analysis showed the following figures: The oil is very dark but fairly clear. It makes in water a dark cream colored emulsion. Ammonia makes this somewhat transparent but it is still far from being clear. The oil contains:

	Sulphonated Cod Oil No. 7 Original oil	Sulphonated Cod Oil No. 8 Calculated for dry oil
Water	19.75	—
Total fatty matter	74.75	93.15
Total SO_3	2.335	2.910
Na_2O	2.407	2.999
Fe_2O_3	0.040	0.050
Ammonia	—	—
Glycerine, impurities and loss	0.718	0.891
	100.000	100.000
SO_3 in salts	0.402	0.501
Combined SO_3	1.933	2.409
Sulpho. fatty acids	9.18	11.44
Oxidized fatty acid	7.82	9.74
Neutral oil (and unsaponifiable)	26.75	33.33
Unsaponifiable	1.35	1.68
Ash	5.14	6.41
Acid value	55.45	69.10
Free fatty acids (as oleic acid) (by titration)	27.91	34.78
Free fatty acids for $M = 300$	29.65	36.94
Free fatty acids by difference	34.98	43.38
Fatty acids in soap	13.02	16.22

0.402 SO_3 in salts =	0.312 Na_2O
1.933 combined SO_3 =	0.749 Na_2O
	1.061
Present	2.407 Na_2O
13.02 fatty acids ($M = 300$) are neutralized by	1.346 Na_2O

	Per cent.
Total fatty matter	74.75
Neutral oil	26.75
Fatty acids	48.00
Fatty acids in soaps	13.02
Free fatty acids	34.98

This does not quite agree with the titration.

The unsatisfactory work again seems due to the amount of free fatty acids being too low and the amount of soap too high.

If we compare analysis No. 8 with No. 6 we see that in No. 8 the acid value is somewhat higher but the amount of fatty acids in soap is almost twice that of No. 6.

Another time I was asked for my opinion of a sulphonated oil and nothing was submitted to me but its analysis. This showed the following figures:

	No. 9 Per cent.
Moisture	26.29
Ash	2.64
Unsaponifiable matter	9.07
Specific gravity of unsaponifiable matter	0.9471
Total oil	66.62
Neutral oil	30.77
Sulphonated oil	35.85
Sulphonation value	53.83
Acid value	41.29
Free mineral acid	none
Emulsion	100.00
Iron	none

Partly neutralized with ammonia.

In his comment the chemist stated that the 9 per cent. of unsaponifiable matter appeared to be a very heavy Texas mineral oil or possibly the unsaponifiable material from a recovered grease. I found out afterwards that the maker of the oil mixed it with 10 per cent. of light mineral oil of 35° Bé.

It was further stated in the comment: "The sulphonation value" which gives a very good indication of the practical emulsifying and driving power of the oil, is lower than is generally found in a good sulphonated oil.

"The moisture is somewhat higher than it should be considering the amount of unsaponifiable matter present."

To make any comment on the moisture test is idle talk as there are very highly sulphonated oils with 50 per cent. water and very poorly made oils with only 20 per cent. of water.

The "sulphonation value" this chemist says, is lower than is generally found in a good sulphonated oil, but we see in the analysis the item

Emulsion 100.00

which probably means that this oil gives an excellent emulsion.

The two terms "sulphonated oil" and "sulphonation value" are entirely erroneous and misleading and without any value whatever as I have proven with sulphonated elaine red oil on page 567 and 568 of the November, 1915 issue of our JOURNAL.

In all analyses of sulphonated oils made by this chemist he fails to determine the most important thing that is the amount of "combined SO_3" which alone characterizes the oil as a sulphonated product and admits a conclusion as to the degree of sulphonation. The figures that are given in his analysis may be obtained from any so-called "soluble oil" made from mineral oil, lard oil, or elaine red oil, with soda or ammonia, alcohol and water.

Now I want to present to you a case that shows the most remarkable discrepancies in analytical work that I ever have seen. It deals with a "fat liquor" that was to be analyzed and matched. As my abilities were questioned and in order to obtain analytical data beyond any doubt, a sample of the same barrel was given to another chemist, who happened to be a university professor. This is what I found:

SAMPLE OF FAT LIQUOR.

The sample is a light cloudy oil with particles like stearine all through it and on the bottom. It sinks in water and when shaken gives a light opaque solution, with a few drops of ammonia it gets clearer, but still remains a little opaque.

	No. 10 Per cent.		No. 11 Calculated for dry oil
Water	53.36		—
Total fatty matter	38.61		82.77
Total SO_3	4 220		9.05
Na_2O	2.614	(= 5.987 Na_2SO_4)	5.61
NH_3	0.012		0.03
Glycerine and loss	1.184		2.54
	100.000		100.00
Fatty matter soluble in petrolic ether	38.04		81.55
Oxidized fatty acids	0.57		1.22
Neutral oil	19.80		42.45
Unsaponifiable	0.58		1.24
SO_3 in salts	1.574		3.375
Combined SO_3	2.646		5.672
Sulpho. fatty acids	12.67		27.16
Ash	6.005		12.87
Fatty acids in soaps	3.63		7.78
Free fatty acids (by difference)	15.18		32.54

1.574 SO_3 in salts combine with	=	1.220 Na_2O
2.646 combined SO_3 " "	=	1.025 "
		2.245 "
Present		2.614 "
Combined in soda soap		0.369 "
0.369 Na_2O combine with	=	3.43 fatty acid ($M = 288.5$)
0.012 NH_3 " "	=	0.20 fatty acid

	Per cent.
Fatty acids in soap	3.63
Total fatty matter	38.61
Neutral oil	19.80
Fatty acid	18.81
Fatty acids in soap	3.63
Free fatty acids	15.18

The total fatty matter is only partly soluble in 95 per cent. alcohol.

Iodine value of unsaponifiable .... $\begin{cases} 47.5 \\ 39.6 \end{cases}$

Total fatty acids (free from unsaponifiable):

Specific gravity at 60° F. 0.9491 =	17.5° Bé
Iodine value	77.4
Saponification value M = 288.5	194.5
Acetyl—saponification value	238.3
" acid value	167.8
Acetyl value	70.5
Titer	21.5

The analysis indicates plainly that the product is a sulphonated oil, made from a vegetable oil, part of which may be castor oil, the rest probably corn oil, mustard seed or rape seed oil.

At the present time there are not sufficient analytical data available to identify the oil after it has passed sulphonation as the fatty acids separated from a sulphonated oil show entirely different figures than those of the original oil. For those who are interested, I recommend the paper by Radcliffe and Medofski[1] who have made a very creditable start in this line. We see from their paper that the iodine value after sulphonation is lower while the titer (solidifying point of fatty acid) is higher, the acetyl value also is higher, but the neutralization value is considerably lower indicating the formation of compounds of higher molecular weights.

[1] "The Sulphonation of Fixed Oils," Soc. Dyers & Col., Feb., 1918. Abst. This JOURNAL.

Now let us look at the other chemist's report:
This oil has the following factors: (Analysis No. 12.)

	Per cent.
Iodine number	47.1
Saponification number	162.0
Acid degree	38.8
Free fatty acids	10.0
Sulphonation	—

This oil is a degras oil. It comes from treating hides as chamois with cod liver oil in the oil tanning process. Therefore, this oil is a mixture of the animal oil, cod liver oil, and combined oxidized oils.

This oil has never been made successfully by combining oils, and is only efficient in fat liquoring as it results from oil tannage.

When I saw these figures and the comment I was surprised that the Professor had not recognized the oil as a sulphonated product and inquired whether there could be any mistake in the samples submitted, but I was assured by eye-witnesses that the samples were identical.

A degras oil, more correctly called woolfat-oleine is a distillation product of woolfat (unfortunately in the United States called "Degras," sometimes "German degras" or "English degras,)" it has nothing to do with cod liver oil or oxidized oils. The real degras, also called "French degras," moellon and sod oil, are originally by-products from the oil tanning process. They contain animal oil, cod liver oil, etc., and their oxidized products and sometimes mineral oil.

A degras oil is insoluble in water and will not mix nor dissolve; a degras or moellon will mix with almost any quantity of water and make an emulsion; a sulphonated oil will dissolve in any amount of water and make a more or less clear solution, or an emulsion which usually clears up and turns into a solution by the addition of a little ammonia.

When I wrote this to the Professor and asked an explanation as to how he obtained his figures he answered that he ran this sample in the laboratory of a friend who spent most of his time on leather research. He admitted candidly that he was not an oil chemist or even a little experienced in that line.

It is to be regretted that he did not say this in the beginning. His friend may be an expert in leather research, but apparently

has never tested a sulphonated oil. It almost appears as a joke when you compare the two analyses, but in the interest of our science it is much to be regretted that these men did not refuse in the beginning to make this analysis, as statements of such discrepancy must lead the laymen to doubt and mistrust our work.

The last example that I want to present to you represents a sulphonated neatsfoot oil which was submitted to me to find out why it did not work in combination with a moellon. Unfortunately any further details were lacking as for a thorough investigation it would have been necessary to know the proportions of all ingredients that were mixed with the oil. The condition of the leather also should have been investigated. I was in the position of a physician to whom only half of the case is told, but was expected to help anyhow. So I had to try the best I could. A full analysis was necessary and these are the figures I found.

The oil makes an emulsion in water which is not much improved or cleared by the addition of a little ammonia.

	Sulphonated neatsfoot oil		
	No. 13 Original Per cent.	No. 14 Dry oil Per cent.	No. 15 Dry oil minus 31% mineral
Water	16.04	—	—
Total fatty matter	48.21	57.41	91.01
Unsaponifiable	31.55	37.58	1.04
Total SO_3	2.093	2.492	3.951
NaO_2	1.095	1.304	2.067
1.095 Na_2O = 2.508 Na_2SO_4			
Ammonia	none	—	—
Glycerine and loss	1.012	1.205	1.910
	100.000	99.991	99.978
Fatty matter soluble in P. E. unsaponifiable	78.00	92.90	88.74
Oxidized fatty acid	1.76	2.10	3.32
Neutral oil	51.04	60.78	—
Unsaponifiable (mineral oil)	31.55	37.58	—
Neutral fatty oil	19.49	23.20	36.80
SO_3 in salts	0.089	0.106	0.168
Combined SO_3	2.004	2.386	3.783
Sulphonated fatty acid	9.52	11.33	17.94
Ash	2.509	2.981	4.736
Acid value	53.1	63.3	100.2
Free fatty acids (M = 288)	27.34	32.56	51.62
Fatty acids in soap	2.32	2.76	4.38
Free fatty acids by calculation	26.20	31.20	49.46

Specific gravity at 60° F. of unsaponifiable 0.8635 = 32.10 Bé.

Fatty acids:

Titer		33.0
Iodine value		44.9
0.089 SO_3 in salts combine with	0.069 Na_2O	
2.004 combined SO_3 " "	0.776 "	
	.845 "	
Total Na_2O present	1.095 "	
Combined with fatty acid	0.250 "	
0.25 Na_2O combine with 2.32 per cent. fatty acid...(M = 288)		

	Per cent.
Total fatty matter	48.21
Neutral fatty oil	19.69
Fatty acid	28.52
Fatty acids in soap	2.32
Free fatty acids	26.20

The figures show the oil is not as highly sulphonated as it should be to carry 51 per cent. neutral plus mineral oil and an additional amount of moellon. If it had a larger amount of soap, it could carry more, as soap helps to hold oils in emulsion, but the amount of soap in this product is rather small.

Another thing that is interesting in this analysis, is that the amount of free fatty acids by titration agrees fairly close to that found by calculation. The reason for this seems to be that in this oil condensation products of low acid value and high molecular weight seemed to be absent. In all the other analyses we have seen differences of from four to six points and always the figures found by titration are smaller than those by calculation based on the amount of extracted neutral oil. There is only one explanation that presents itself: On account of deeper going changes of the fatty acid molecule that have taken place during the sulphonation process there are such oxidized, polymerized or condensation products like anhydrides, inner anhydrides, lactones, lactides, etc., present, that cannot be reached by titration nor by extraction with ether. As petrol ether is not such a good solvent it is natural that the differences become still larger if an extraction with petrol ether is made. We really make the biggest mistake if we express the free fatty acid as oleic acid, our figures will always be too small, as inner anhydrides with an acid radical (COOH) on one end of the chain are present that have a molecu-

lar weight in the neighborhood of 562, about twice that of oleic acid. Even if we do not investigate this matter any further we know that these products that we cannot reach and determine separately by a simple method, must be some products created by *further action of the sulphuric acid on sulphonated fatty acids* decomposing them to oxidized and polymerized compounds, which very likely have a beneficial influence on leather. As we understand that the term "neutral oil" signifies the unaltered portion of a sulphonated oil, we can, without making any mistakes, let the matter rest by adopting the extraction with sulphuric ether for the determination of "neutral oil."

Before I close I want to mention another question that seems of common interest. I have been asked frequently whether a sulphonated oil contains any free sulphuric or mineral acid and how it could be determined. I suppose that you all are familiar with the process of sulphonation in general. You know that after the action of the acid on the oil, the bulk of free sulphuric acid is removed in the washing process. The oil which still contains some acid water and Glaubersalts is treated with a solution of soda, potash or ammonia. The mineral acid, while stronger than any organic acid, will first take the alkali until every bit of it is neutralized, the next to be neutralized are the sulpho-fatty acids and the last the free fatty acids; of the latter usually only a part is neutralized. There is no chance for mineral acid to remain unneutralized.

Sulphonated oils that are only washed but not neutralized are used in certain dyeing processes, but as these products do not keep they are usually made shortly before they are used. Probably because such oils are not a marketable product, text books never mention a test for free mineral acid. Such a test could easily be made by extracting in a separator 50 to 100 grams of sulphonated oil dissolved in 250-500 cc. sulphuric ether with a concentrated neutral solution of sodium chloride or sodium sulphate. The brine usually will soon settle perfectly clear and water white, and then can be drawn off and tested for free mineral acid.

If a sulphonated oil contains much water, it happens that the brine gets too diluted and remains yellow or cloudy. This can be remedied by the addition of more concentrated brine, until after

another shaking, a clear salt solution settles from the ether. For quantitative tests several extractions will be necessary.

I hope that my remarks will lead to further investigations. We really are not in a position yet to say which items of the analysis of a sulphonated product indicate the most desirable ingredients; are these the sulpho-fatty acids or are they the products resulting from further action of the sulphuric acid on the sulpho-fatty acids, products of decomposition, condensation and oxidation? I have seen good results with oils high and low in combined SO_3, was there anything else in these oils that brought the good results about, that has escaped our attention? Perhaps the oil with high content of combined SO_3, could have been used more sparingly and, therefore, more economically with the same good results; or were these results due to the products of oxidation and condensation for which a simple method of determination is still lacking? It even remains doubtful at the present time whether the action of all these different constituents of a sulphonated oil are more of a chemical or more of a physical nature. Close observation combined with exact analytical work is necessary for any progress in this line but such observation can only be obtained by perfect co-operation between tanner and chemist.

LABORATORY OF F. S. WALTON CO.,
May, 1919.

ABSTRACTS.

The Testing of Sodium Bisulphite in the Laboratory of the A. V. R. O. S. By F. C. VAN HEURN. *Arch. Rubbercult, Néederland. Indië* 2, 12; *Meded. Alg. Proefstat. Alg. Ver. Rubberplanters Oostkust Sumatra, Rubber Ser.* No. 6, 12 (1918) *Expt. Sta. Rec.* 39, 413; C. A. 13, 1064 (1919).

Technical samples of sodium bisulphite generally contain in addition to the bisulphite itself, some Na_2SO_3 and Na_2SO_4. In dissolving samples for analysis the $NaHSO_3$ becomes $Na_2SO_3 + H_2SO_3$. Taking this into consideration the following method of analysis has been developed: About 1 gram of the material is weighed in a weighing tube and a small quantity of water added, the solution is poured into a graduated glass stoppered volumetric flask and made up to 1 liter. This solution is used for all determinations. To determine the amount of SO_2 present as bisulphite, 100 cc. of the solution is placed in an Erlenmeyer flask and

titrated with 0.1 N KOH using phenolphthalein as an indicator. Double the quantity of SO_2 found is present as bisulphite. This amount multiplied by 1.63 $\left(\frac{NaHSO_3}{SO_2} = 1.63\right)$ gives the maximum amount of $NaHSO_3$ that can be present. To determine the total amount of SO_2, some of the original solution is placed in a burette and titrated with 25 cc. of 0.1 N iodine solution. The amount of SO_2 present as normal sulphite is then found by subtracting from the total SO_2 the amount present as bisulphite. To determine the amount of sulphate 100 cc. of the solution is placed in an Erlenmeyer flask and 1 cc. of concentrated HCl and a few drops of alcohol are added. The air in the flask is replaced by CO_2, and the solution is heated and precipitated with a 10 per cent. solution of $BaCl_2$.

Formic Acid and Mercuric Chloride Treatment of Hides Affected by Anthrax. V. GEGENBAUER. *Arch. Hyg.*, 1918, 87, 289-315. *Chem. Zentr.*, 1919, 90, II., 132-133. *Abst. J. S. C. I.* 38, 429A (1919). The Seymour-Jones process for the sterilization, by means of formic acid and mercuric chloride, of hides effected with anthrax, has been subjected to a series of trials. Experiments were made following the technique of Ottolenghi with mercuric chloride solutions of 0.1, 1.0, and 2.0 per cent. strength, which effected sterilization only after 80 days, and with a 0.01 per cent. solution which required 100 days. A solution of 0.02 per cent. strength in combination with 1, 2, or 5 per cent. of formic acid did not sterilize in 40 days. Growth was obtained in albumin bouillon after 100 days' action of a 1 per cent. solution of mercuric chloride. Growth was also obtained from anthrax spores (from which all traces of mercuric chloride had been carefully removed by centrifuging and decanting, but without treatment with sulphides) after the spores had been subjected to a 0.01 per cent. solution for 20 days, to a 0.1 or 1 per cent. solution for 8 days, and to a 2 per cent. solution for 2 days. In the same series of experiments growth of the spores could still be observed after 8 days' action of 0.025-0.10 per cent. solutions of mercuric chloride, and 4 days' action of a 1 per cent. solution in combination with 1 per cent. formic acid. After the action of hydrogen sulphide solution on the spores and subsequent washing, 1 per cent. and weaker solutions of mercuric chloride together with 1 per cent. formic acid did not effect sterilization even after 14 days. Anthrax spores treated by the Seymour-Jones method proved pathogenic when introduced into guinea pigs. The conclusion is that for practicable concentrations and times of action the method is in no way effective.

Tannin and the Synthesis of Similar Substances. E. FISCHER AND M. BERGMANN. Ber., 1919, 52, 829-854. *Abst. J. S. C. I.* 38, 429A (1919). The removal of acetyl groups from substances such as the acetates of galloyl- and digalloyl-glucose, previously effected with cold alkali or with warm sodium acetate solution, can also be effected at the ordinary temperature by a moderate amount of concentrated aqueous hydrochloric

acid in methyl-alcoholic solution. If the acetyl-derivative is too sparingly soluble in methyl alcohol, a mixture of the latter with acetone may be used. The penta- (*m*-digalloyl)-α- and -β-glucoses obtained in this manner from the acetates are optically purer than those previously described. The method can also be applied with good results to simpler substances such as acetylsalicylic acid and triacetylgallic acid. The use of the potassium salt for the purification of tannins was recommended by Berzelius; the authors find the most convenient method of preparation to consist in mixing alcoholic solutions of the natural or synthetic tannins and potassium acetate, but the precipitates contain small amounts of the latter. The salts appear to be suitable for the purification of artificial tannins but not for their identification. Attempts to extend the method used in the preparation of 1-monogalloyl-β-glucose (*J. S. C. I.* 38, 47A 1919) to other 1-acylglucoses gave disappointing results, the acyl-group being frequently removed simultaneously with the acetyl groups. This is the case, for example, with 1-benzoyltetra-acetyl-α-glucose, but not with the corresponding *p*-hydroxybenzoyl-derivative. The catalytic action of sodium alkoxide on esters in alcoholic solution has been applied for the removal of acetyl groups. Thus, for example, for the elimination of the five acetyl groups of *p*-acetoxy-benzoyl-tetra-acetylglucose dissolved in alcohol, 1 molecule of sodium ethoxide is sufficient at the ordinary temperature and the presence of a small quantity of water in the alcohol does not hinder the reaction; these conditions are particularly advantageous for securing good yields. The method has also been applied to the isolation of glucose from its penta-acetate and of α-methylglucoside from its tetra-acetate. The galloyl-derivatives of the sugars differ considerably in their behavior towards gelatin solutions. The penta- and tri-galloyl compounds precipitate the latter from aqueous solution in the same manner as do the tannins, but this property is not shown by the various monogalloyl-glucoses nor by monogalloylfructose. Since similar differences were to be expected among poly-hydroxy-alcohols, the derivatives of glycol, trimethyleneglycol, glycerol, erythritol, and mannitol have been prepared and examined. The crystalline ethylene-glycol digallate is so sparingly soluble in water or alcohol that its reaction with gelatin or arsenic acid could not be investigated. With trimethyleneglycol digallate the gelatin test is not characteristic but distinct gelatinization is caused by arsenic acid in alcoholic solution. Erythritol tetragallate is readily soluble in water and coagulates gelatin, but the alcoholic solution is too dilute to be tested with arsenic acid. The amorphous glyceryl trigallate and mannitol hexagallate yield colloidal solutions in water and behave like tannins towards both reagents. (See also *J. Chem. Soc.*, 1919, i., 278.)

Examination and Valuation of Military Leather. E. Seel, K. Hils and K. Reihling. Z. Angew. Chem., 1919, 32, 4-7. Abst. *J. S. C. I.* 38, 431A (1919). German military leathers and others from prisoner's camps in Germany were analyzed in considerable numbers. Only Russian leathers proved to be under-tanned; French and Serbian as well as German leathers were well tanned. The combination color reaction de-

scribed by Hundeshagen (*Chem. Zentr.*, 1902, II., 752) is considered superior to the usual glacial acetic acid test for detecting under-tanning. None of the leathers examined proved to be weighted with inorganic materials, the mineral ash ranging from 0.5 to 1.5 per cent. Sulphates were present only in traces. Little sugar was found in the leathers, the highest amount being 1.4 per cent. after inversion. A feature of the analyses is the large number of positive tests for artificial tannins, in particular for Neradol D; only in three cases was artificial tannin absent from the German leathers. Ordoval G, a product introduced by the Badische Company during the war, was not once detected. A comparison was made between Neradol D, Neradol ND, and Ordoval G as follows:

	Litmus	Congo red	$BaCl_2$	$HCl + BaCl_2$	Filtrate from previous pptn. boiled 2 hours under reflux
Neradol D....	Red	Blue-violet	Ppt.	Considerable ppt.	Ppt.
Neradol ND ..	Red	Pure blue	Ppt.	Extremely slight ppt.	No ppt.
Ordoval G ...	Red	Blue-violet	Ppt.	Very slight ppt.	No ppt.

The authors make several observations on the necessity for the absence from military leathers of free sulphuric acid, which was found in several instances.

The Fancy Leather Workers of Djokjakarta. C. E. Bosworth. *S. & L. Rep.*, July 24, 1919. Hidden in the heart of Java are ruins and arts so ancient that the antiques of the so-called "old world" often assume a modern aspect in comparison. Like most of these wonders, Java's show the influence of ancient religions. Of particular interest to us are the members of a small cult of workers in fancy leather who carry on their trade in and around Djokjakarta thereby perpetuating an industry which once spread throughout Java. I can find no treatise, lengthy or otherwise, which explains this particular art, but in 603 the Indian Prince, Guzerat, came to Java with 5,000 followers and established a Buddhistic influence which endured for several centuries almost unrivaled. Along in the ninth century the great temple of Tjandi Boroboedoer (shrine of the many Buddhas) was built a few miles from Djokjakarta by the descendants of these immigrants and their converts. Although built of lava rock and without cement or mortar, this temple has endured through the centuries, and stands to-day a monument to that ancient civilization more wonderful in its bas-relief and whole symetry than any other Buddhistic ruin. About the time of its completion, the influence of Buddhism began to decline with the advent of the Hindoos. Unquestionably, this working in fancy

leather was brought to Java either by the early Buddhists or by the Hindoos, more probably by the former, for some of these leather workers still go to the ancient temples at Boroboedoer and to the smaller but none the less ancient at Brambanan, to worship. Also, there is a certain similarity between this leather work and that still carried on in the south-east of India, where gaily colored ornamental harnesses are made for the bullocks used in ceremonial processions and the like. The products of these cults in both India and Java are absolutely useless and perhaps serve as a further illustration of the perverseness of the east. These peoples have never used leather of their own making until very recent years for anything for which leather is used by the rest of the world. Also, even though now using leather to a limited extent for its customary purposes, these peoples make no effort to produce a leather of quality for service, but they still show wonderful skill and infinite pains in producing their fancy leathers.

It is almost in the shadow of these temples of Boroboedoer and Brambanan that the few perpetuators of this ancient industry still work. The raw material is the hide of the Asiatic water buffalo—the ubiquitous beast of burden throughout the east. Except under the eye of a watchful white man, the hides are not flayed with any particular care but as soon as they are removed from the carcass they are stretched in a rectangular framework of stout bamboos and thoroughly dried in the full glare of the tropical sun. After this first drying, they are soaked in any convenient water—river or irrigation ditch—until thoroughly pliable and then painted with lime. When the hair slips easily, they are again stretched on the drying frames and the hair removed by scraping. The next operation is quite surprising. In Java and Madoera there are something like 560,000 Chinese and the Chinese civilization in Java is centuries old. Also, the Chinese have used the hide of the buffalo for ages and it is their usual custom to split it by hand into sections of the desired thickness. Some people familiar with the industry in China say that a single hide is often split into from ten to fourteen sheets. This seems almost too many to be possible considering that the work is done by hand but my informants ought to know. I have never seen more than five splits from one hide. Four of these were practically perfect—the fifth showed the irregularities of the hides. Despite this chinese influence, the Javanese do not resort to splitting. The hide is usually cut into convenient sized pieces and then stretched in a small frame and scraped to the desired thickness. After the hide is thus reduced, it is again thoroughly washed and given its final drying.

The actual decorating and cutting of the leather is really the most interesting operation. The piece to be decorated is laid on a cutting block before which the decorator kneels for hours and patiently punches the intricate designs. In nearly every piece of purely native design the Wayang is the central figure. The Wayang is the native Javanese actor and there are about one hundred and twenty of them necessary for each performance. In reality the Wayang is a doll of either wood or leather,

mounted on a stick or piece of buffalo horn. In either event the personality of each "character" as to shape and color is the same. The arms are jointed and attached to the hands are sticks to make their operation possible. The performance consists of an operator who works these dolls in illustration of the tale unfolded by the storyteller to the accompaniment of the weird Javanese orchestra. It is really a shadow show. But as with other peoples, the theatre and its characters play such an important part in the lives of the people that the Wayang finds its way into nearly all native art. In addition to the Wayang we find the peacock though this is probably a more or less modern innovation. These central figures are accentuated by a field or ground work of wonderfully fine and intricate patterns—lace-like in detail. A skilful worker cuts the design in the hide withhout any preliminary drawing but the less skilful first trace their patterns. The tools used are of native manufacture long handled, circular, semi-circular, or square shaped cutting dies remarkably small and keen. These dies are struck with a small wooden mallet. No dies are used which will cut a complete pattern.

Utilization of Spent Bark. From *le Progress agricole,* through *la Halle aux Cuirs,* June 8, 1919. Two practical uses for spent bark are noted. It is valuable as stable litter, since it absorbs liquids and gases and its fermentation acts in opposition to that of manure. It may also be used as fertilizer; it tends to produce a granular soil and contains from ½ to 1 per cent nitrogen, traces of phosphates, potash, and from 3 to 4 per cent. lime. J. A. W.

Problems of Evaporation and the Manufacture of Tanning and Dyeing Extracts. J. A. Reavell. *Lea. Tr. Rev.,* June 11, 1919. The object of this paper is to describe the various processes and operations that take place from the arrival of the raw material into the factory to the production of the tan extract in its finished state. The final product may be either a concentrated liquid or a solid extract. The raw material may be either green or dry, depending upon the position of the factory relative to the supplies. The first stage of the process is the disintegrating, crushing or grinding of the bark. The ground material is then conveyed to the leaches, or vats, where the actual extraction of the tan takes place. This liquid extract passes forward to the evaporator where the water is removed and a concentrated extract produced containing about 30 per cent. to 40 per cent. tannin, or if a solid extract is required, this concentrated liquor is then carried forward to a finishing evaporator.

Bark Crushers.—The bark or nuts must first of all be crushed before being dealt with in the leaches. There is obviously a considerable amount of discussion and competition among the various makers of bark crushers or grinders, as to who can produce the machine best suited for this work. The question is at once raised as to how fine it is necessary to crush or grind the bark, or raw product, and it can be definitely stated at this point that the finer the bark is ground, the greater the ease with which the

extraction of the tan can be made; but there are other difficulties that arise if the bark be ground too fine. With extremely fine grinding, the leaches are clogged and something in the nature of a slime is formed, which blocks up the sieve arrangements. It also makes it more difficult for the water to get into intimate contact with the bulk of the material, which is in the leach itself, so that a compromise is made, and the grinding is as fine as will avoid this difficulty.

In fine grinding, particularly with dry bark, a considerable amount of dust is produced, and it is very important that this dust should not be lost. It has been found, when samples of dust have been analyzed, that while the bark itself may contain 33 per cent. of tan, the dust can contain 46 per cent. of tan. This indicates clearly enough the necessity of recovering all the dust, and extracting the tan therefrom.

In order to emphasize the point that the degree of grinding makes a material difference to the extraction of the tan from the bark, assuming the duration of leaching, temperature, etc., remain the same, the following is a set of figures showing the amount of tan contained in the spent bark removed from the leaches when varying degrees of grinding are adopted. The first figure is obtained with unground bark and the last with very finely ground bark:

Percentage of tannin in spent bark and calculated as containing the same moisture as the original charge:

Chopped bark (unground)	8.7
Closely-ground bark	8.3
Medium-ground bark	6.8
Finely-ground bark	6.1

Conveyors.—After the bark has been crushed it is necessary to convey it to the leaches. To do this various types of conveyors have been adopted. While the raw material can be conveyed very easily in any ordinary type conveyor, it must be borne in mind that, under certain conditions, owing to the nature of the product only copper or wood should be used in the construction of the apparatus. The best plan is to take the bark, or other material direct to the crushers by means of a conveyor, and arrange the crushers at a higher level than the leaches, so that the ground material can be dumped through chutes into them. This meets the problem of mechanically handling the ground bark, but it is one of the points that must always be decided by local conditions.

Leaching.—The main object that one has in mind in the process of leaching is to bring the water in contact with the bark in such a way that the whole, or as much as possible, of the soluble tan is removed, and in doing this to keep the labor involved down to the absolute minimum. The perfect method of leaching is one in which the ground bark travels in one direction while the liquid travels in the opposite direction, so that the fresh water enters where the spent tan leaves and the liquid leaves where the fresh bark enters. The tanners have produced their own liquor, which

they have used as thin liquor, for many years, and have generally extracted the tan from the bark by using their tan-pits as leaches. By this system it takes from 4 to 6 weeks to complete the extraction, the reason being that the circulation is very poor. The system is not in any way a good one, as the pits were never designed for this purpose. They are extremely difficult to empty, in fact, in the present time of labor scarcity, it is almost impossible to get men to tackle this class of work. It is agreed by all practical men that this system will have to be abandoned altogether. One of the first things to bear in mind is that the leaches must be accessible. They must be designed so that the crushed bark can be readily charged into the leaches and the spent bark easily removed therefrom.

There are various systems of leaching at the present time:

1. The open type vat. This vat may be round or square and varies in height, but the principle is the same throughout. It is generally constructed of wood, though concrete and other materials have been used.

2. The rotary system. This has been used very little so far, but the impression is that this is a system which should be developed further as it has a great many valuable features.

3. The pressure auto-clave system.

4. An open type trough containing an archimedian screw.

5. Leaching under pressure and vacuum.

6. Extraction by rollers.

The chief feature of the original leach or vat was a perforated plate about 12 inches from the bottom of the vat. This perforated plate is usually of copper, arranged so that the liquor only passes through. The method of operating is, first of all, fill up a few inches above the false bottom with water or liquor from another vat, then begin to charge with ground bark, adding the rest of the water as the bark is thrown in. In order to heat the leach a copper perforated steam coil is placed in the lower portion of the vat below the perforated plate. A copper coil is employed, arranged with a series of perforations about 3/16 inch diameter. The steam is then turned on, the effect being to agitate the liquor and heat it at the same time. But the liquor is very considerably diluted by the steam condensing, which means that greater evaporation has to be carried out.

In another type the heating is carried out by means of a separate heater, or calorifier. The object of this is that the liquor in any one of the leaches, or vats, can be increased in temperature without decreasing its density. The method of operation is to open one of the valves at the bottom of the leach, which couples up to the connecting pipe of the centrifugal pump, and discharges into a wooden trough that is placed above the leaches, so that if it is desired to increase the temperature of the liquor in any one vat, this is done merely by circulating the liquor for a given period through the calorifier. This system not only heats the liquor without decreasing the density, but it also has the advantage of creating

a positive circulation in a correct direction. By blowing steam into the liquor in the bottom of one of the vats, it not only lowers the density of the liquor, but it does not give a definite circulation. It is true that hot water rises, but this is a case where you have a relatively thin and clear liquor at the bottom, where the steam is being blown in, but above it, is a mass of ground bark floating about in the liquor, and the heat does not readily pass through this product. Thermic circulation alone cannot be depended upon in such cases. The bad effect of blowing steam directly into the liquor may be better appreciated by taking a concrete case: Vat containing 9 tons of liquor to be raised in temperature from 20° C. to 90° C. (68° F. to 194° F.) in 1 hour, steam being supplied at 30 pounds pressure. Allow 10 per cent. for losses, the steam required would be roughly 1.35 tons. The steam being condensed and added to the original quantity of liquor brings it up to $9 + 1.35 = 10.35$ tons, or diluting the original liquor by 15 per cent. This added condensed water has to be re-evaporated in the evaporator, materially increasing the steam consumption of the whole plant, and, when working the evaporator under vacuum, throwing more work upon the air pump. With the use of the calorifier and by pumping the liquor round, the liquor itself becomes heated and a definite circulation is obtained, which has the advantage of stirring up the bark and giving a good mixing effect.

The rotary leach consists of a series of drums, each about 8 feet long and 6 feet diameter. They are operated in the same way as a series of vats, but have the advantage that a much more intimate contact of the liquor and the bark is obtained, therefore a more perfect extraction. Counter-current working is adopted, exactly the same as in the vats the liquor passing from one drum to the other the bark remaining in the drum, and being washed by a series of waters, the exact number depending on the number of drums. To charge the bark a drum is stopped in such a position that the opening is at the top. The bark is dropped through this opening by means of a chute. The cover is then secured, and the liquor from the previous drum is discharged into it, so that a new charge of bark receives the last series of liquor. The method employed is to run the liquor from the previous drum into a tank, and pump this back either through the calorifier, or direct, depending on the temperature required. This operation is repeated on the other drums. To empty the liquor, stop the drum and open the valve. As soon as the liquor is drained off, the door is opened, and the spent material thrown down into a truck placed immediately below. If necessary, the drum is rotated to facilitate the removal of the spent material. Now that labor is getting more and more costly, and seeing that the problem of handling the bark, especially the spent bark, is difficult; there is no doubt that either this, or some mechanical form of leaching will have to be adopted.

Pressure autoclaves were in vogue for a long while particularly on the Continent, but are being gradually abandoned. There is no doubt that the idea of the pressure autoclave was copied from the beet sugar industry.

The vessels are constructed of copper and are obviously very expensive. A hinged door is arranged on the top and at the side of each autoclave for filling and emptying, steam connections being provided for heating. The steam is blown directly into the liquor and gradually the pressure is increased until about 30 pounds is reached. The leaches are worked on the counter-current principle. To charge an empty vessel from a full one, steam pressure is applied to the full autoclave, and the liquor blown up into the empty autoclave.

There is a system of vacuum leaching known as the Nance System, which follows the pressure type of autoclave, except that it has a vacuum on the vessel. There is not much known as to the results obtained by this system.

As the beet sugar industry on the Continent affected the extract industry, so in the Colonies the cane sugar industry has affected the extract manufacturer, hence the system of leaching known as the Bilborough and Frew process. The bark is crushed in the normal type cane crusher with Krajewski rollers. A Mr. John Kirkman, many years ago, made experiments with wooden rollers to crush the bark before going to the leaches. He claimed to have obtained satisfactory results.

Open Trough and Screw.—A German firm, Riedler & Peratonaer invented a system of leaching which has been adopted a good deal abroad, and in this country. It consists of a long trough built of wood, in which is placed an archimedian screw, of copper and brass. The new bark is fed in at one end and carried forward by means of the screw, the water passing counter-current, and leaching taking place in the usual way. The spent bark falls into a hopper, from which it is thrown out by means of elevators. There are, however, difficulties in this method of leaching, due to the jamming of the screw and the removal of the bark. It has given excellent results on some materials.

The method of operating a battery of leaches is described as follows: Assuming there are eight vats working normally, and that vat No. 4 is the one from which the spent bark is next to be removed and the new charge of bark put in, the liquor is first drained out of No. 3 and taken to the evaporator, No. 3 being the last of the series which contains the fresh bark. Then No. 3 having had the liquor run off, the liquor from No. 2 is pumped into No. 3 (it can either be pumped through the calorifier or by-passed, depending on its temperature). The liquor from No. 1 is put into No. 2, No. 8 liquor into No. 1, No. 7 into No. 8, No. 6 into No. 7, No. 5 into No. 6 and No. 4 into No. 5, thus No. 4 is the leach emptied of its liquor and containing only bark that has had eight sets of water over it. Having thoroughly drained the liquor from No. 4 the door is opened and the spent bark removed. The vat is then ready to receive the new charge of bark. A new charge of bark is put in and the liquor pumped from No. 3 to No. 4, that is, over the new bark, from No. 2 to No. 3, No. 1 to No. 2, No. 8 to No. 1, and so on. No. 5 is pumped into No. 6, leaving No. 5 empty of liquor. Fresh water is now pumped into No. 5, and usually kept at a temperature of about 100° C. This is easily done by circulating through the calorifier.

Generally speaking, the last bark is kept at a high temperature, so that it can be thoroughly spent before being thrown out, and the temperature grows less towards the time when the liquor is meeting the fresh bark. This gradual cooling of the liquor while passing over the material, tends to give much clearer liquors as different soluble substances extracted at high temperature gradually precipitate and are filtered out in the fresh bark.

The tanner reckons that 1 per cent. more tannin is extracted by actually boiling the last leach than by working at temperatures much below 100° C. It is, however, admitted that high temperatures, if used on fresh material, destroy the tannin.

A question that is always asked in regard to leaching is: What is the best shape and size of a leaching vat? The size of the leach is determined very largely by the space available, and also the ultimate time of contact that is required to spend the bark. The minimum number of leaches that should be used is six, that is based on the use of normal labor; although a very successful system is at work, producing considerable quantities of extract with only three leaches. The question arises as to how much liquor can be produced per ton of bark and what is the density of the liquor so produced? The answer to this question, obviously, is that it depends upon the method of leaching, and also upon the amount of tannin contained in the raw material. But assuming that a good commercial type of leaching system is adopted, and taking an average material, myrobalans, mimosa or similar barks, it can be admitted that 670 to 700 gallons of liquor at 45° B., that is, a specific gravity of 1.045 at 60° F. can be obtained per ton of bark. This is equivalent to about 9 per cent. of tannin by analysis.

The next question that is asked is how much tannin is left in the spent bark? Extract manufacturers are much more particular than the tanners in this respect. They extract the absolute maximum that can be obtained commercially from the bark. But it should be borne in mind that manufacturers in this case produce their product with a view to obtaining the maximum amount of saleable matter, whereas the tanner who manufactures for his own use has other objects in view, he wants to get the purest extracts to use in the tanning of his leather. Whereas the manufacturer claims to extract to under 2 per cent. of tannin left in the spent bark, the tanner seldom extracts down to 5 per cent. This 5 per cent. does not mean that with a bark containing 33 per cent. of tannin only 28 per cent. is extracted, as the 5 per cent. is calculated as the amount of tannin remaining in the spent bark and not on the original bark.

To put it more clearly, if 100 tons of bark are put into the leaches and 45 tons of tannin extracted, there will only remain 55 tons of bark of the same moisture, and it is on this that the 5 per cent. is reckoned. It is equal to about 2.75 per cent. of tannin on the original bark. In actual practice, 100 tons of mimosa bark of average good quality will yield 100 tons of liquid extract containing 30 per cent. of tannin.

There are two other points of interest in regard to tannin extract. First, the effect of heat in regard to acidity. With mimosa it is necessary to add acid to the liquor, as it contains very little volatile acids or sugar-yielding material, or else to use myrobalans in conjunction with it. Secondly, there is the question of the prevention of fermentation. In normal weather conditions, ½ per cent. of bisulphite of soda is used to prevent fermentation, but in the case of higher temperature this is not sufficient, as mimosa readily develops a yeast which ferments the sugars, and it is necessary to add 1 per cent. cresylic acid.

The question arises as to what can be done with the spent material. It is bulky and expensive to handle if the works are in a town, where it must be carted. The product contains a considerable amount of moisture, and on the whole is undesirable material. It can, however, be used for burning in the boilers. To do this a special grate must be attached, as the ordinary type grate cannot be used for this purpose. What is known as a step grate is adopted, and if the product is left to drain, particularly if it can be left exposed to the air, it can be quite well burnt together with a certain amount of coal and produces a good fuel. Sometimes this spent material is passed through rollers in order to remove the excess water, but the calorific value is so low that we must bear in mind that one of the reasons, if not the only reason, of burning this is to get rid of it. In any case, a certain amount of coal must be mixed with it for burning. The other uses to which this spent bark can be put are (1) for the production of producer gas, and (2) spent bark has also been used for paper-making, but produces an inferior quality of brown paper. The quality was greatly improved by the addition of a small percentage of fresh bark.

Evaporation of Tan Extracts. The liquor as it leaves the leaches is a thin liquid containing about 9 to 10 per cent. of solids. If the extraction is good it is as high as 10 per cent., but 9 per cent. can be taken as an average figure. In order to concentrate this to produce the standard extract it is necessary to evaporate the water so that there is a content of about 38 per cent. to 40 per cent. solids in the concentrated liquid. This means an evaporation of 78 per cent. to 80 per cent. of water. For instance, in 100 tons of liquid containing 9 per cent. solids 80 tons of water have to be removed in order to give the 20 tons of liquor required at 40 per cent. solids.

If we take a concrete example and assume that 50 barrels of extract are required at 40 per cent. solids, this is equivalent to 10.5 tons of liquor at 40 per cent., or 180° B. Assuming that you have the thin liquor at 9 per cent. solids, it will be necessary to evaporate 36.3 tons of water. The problem, therefore, that has to be considered is how to economically evaporate this 36 tons of water, as it is a material expense in the manufacture of tan extract.

The first type of pan in which vacuum was applied in order to reduce the boiling point was one invented by an Englishman named Howard,

an ancestor of the present Duke of Norfolk. The natural evolution from this jacketed type pan was the coil type pan. The great advantage over the previous types is, of course, the application of a vacuum. A more modern type is the single effect vacuum pan. From the ordinary single effect type pan the multiple effect naturally followed. The industry, however, found that even though the temperature was reduced by the application of vacuum, still the liquor was not as satisfactory, from the point of view of color, as it might be, and reference showed that even at low temperatures the fact that the liquor was in contact with the heat for long periods, as it must be in the open type pans was detrimental. Moreover, in the first effect of a triple pan, the liquor not only remains in the pan for a long period, but it is actually subject to a high temperature.

Other types of evaporators were, therefore, developed, particularly the "film" type. One of the best known of these is the Yaryan. Another type of horizontal evaporator that is very well known is the Kestner horizontal film. It will be seen, however, that the horizontal "film" has distinct disadvantages, inasmuch as it is practically impossible to get a perfect film the whole length of the tube, the effect of gravity being such that the liquor tends to travel rather along the lower portion of the tube than remain in a film round the inner surface. It was for this reason that Mr. Kestner in his great invention of the climbing film sought some method of film evaporation which would, under all circumstances give the perfect film.

The main objects to look for in an evaporator dealing with this particular problem of evaporating tannin extracts are:

(1) The evaporation of the maximum amount of water with the minimum amount of fuel.

(2) Short contact of the liquor with the heating surface.

(3) Prevention of loss by entrainment or frothing.

In regard to the first point, *i. e.*, economy, it may be said that in modern evaporators there is not a great deal of difficulty in the actual efficiency of the apparatus when working under the best conditions, that is to say, assuming that you have a liquor that does not scale, and providing time contact is not detrimental to the product, there is not a great deal of difference between the different types of evaporators. It is also admitted that the way to obtain economy is by working the maximum number of effects. The number of effects that can be operated depends largely upon the temperature drop or temperature head under which an evaporator will work. This is almost analogous to the head required to cause water to flow through a pipe. For instance, if the temperature of the heating steam is 110° C., and the temperature of the vapor in your evaporator is 50° C., there is a difference of temperature of 60°, which causes the heat to be transmitted from the steam through the walls of the tube to the liquid to be evaporated. If you have three effects, this gives you 20° temperature head for each effect. If, however, you are able to work your evaporator on a very low temperature head,

you can reduce the temperature of the heating steam used in the evaporator. This is naturally a very important point when dealing with liquors like tannin extracts which are sensitive to heat. The Climbing Film Evaporator has been found in practice to work with a lower temperature head per effect than any other type, so that on the first count the "film" evaporator gives a very material advantage.

The second point is the question of time contact. It will be admitted that this is of enormous importance, because, however low the temperature is, if the liquid remains in contact with the heating surface so that stewing takes place it is bound to materially affect the product in spite of the low temperature.

It is necessary, therefore, to design an evaporator so that the liquor instead of circulating within the pan or evaporator must pass directly through it in one direction only. This is accomplished either by a horizontal or a vertical film evaporator so that from the point of view of time contact the film type evaporator must be adopted. It is also evident that the vertical film gives more satisfactory results than a horizontal because the film is not in any way interfered with by gravity, and can be perfectly maintained, however thin it may be.

The third point, namely, entrainment or the loss of liquor due to frothing, is a most important one, particularly when dealing with valuable liquors. In the ordinary pan it is impossible to prevent frothing if anything like the maximum duty is demanded from the heating surface. In fact, wherever you have a bulk of liquor any change in temperature will create the frothing. In a "film" evaporator the quantity of liquor is always very small. The evaporation takes place at a regular rate, and consequently it is only a question of calculation to determine the speed of the vapors and design the separator so that there is no loss due to entrainment. In many cases losses of valuable products will amount to as much as 5 per cent. or more of the product treated per day.

The principle of multiple effect evaporation is that by means of alternate evaporation and condensation the latent heat is exchanged successively as a means of separating water from solids. In order to show the advantages gained by this multiple effect evaporation the following table is given:

COMMERCIAL FIGURES FOR WATER EVAPORATED PER 100 UNITS OF STEAM.

Steam 100	Single	Double	Triple	Quad.
Water	95	150	220	300

COMMERCIAL FIGURES FOR WATER EVAPORATED PER 100 UNITS OF COAL.

Coal at 6 = 1.

Coal 100	Single	Double	Triple	Quad.
Water	570	900	1,320	1,800

EXAMPLE 1,000 KILOGRAMS OF WATER EVAPORATED IN TRIPLE EFFECT.

(*a*) Steam required $= \frac{1{,}000}{220} \times \frac{100}{1} = 450$ kilograms.

(*b*) Coal required $= \frac{450}{6} = 76$ kilograms.

You will see that, assuming your boiler is evaporating 6 pounds of water per pound of coal with a single-effect evaporator, 570 tons of water can be evaporated for 100 tons of coal. With a triple-effect 1,320 tons of water can be evaporated for 100 tons of coal.

The object of multiple-effect evaporation, you will notice, is merely to reduce the cost of removing the water. One is often asked what is the maximum number of effects that should be adopted. The answer is that each case must be determined on its own merits.

In the case of tanning extracts the question of capital cost is a material consideration, seeing that all parts have to be constructed of copper, but in these days of expensive coal, and when there is a likelihood of its being even more expensive the problem of economy in evaporation will become more and more important.

One of the methods of producing solid extract is by concentrating it in a vacuum pan. The difficulty in regard to this, however, is the question of the circulation of the liquor and the long-time contact. It is true pumps have been used for circulating the liquor round from the bottom of the pan and spraying it on the top of the tubes, but this has never proved a successful method as the sprays to be effective must have very fine nozzles which in turn readily become blocked. A method has been adopted by vacuum pan makers in order to obtain this circulation. In some cases a large central tube is built. The circulation is usually obtained by means of an archimedian screw. The liquor is forced downwards by this screw and upwards through the evaporating tubes, thus a positive circulation is obtained. In some designs, instead of putting the Archimedian screw on the outside of the pan it is fitted inside and placed in the central tube itself. But whichever method is adopted it is obviously a very expensive and cumbersome form of apparatus to adopt, and requires a very large heating surface for the relatively small amount of evaporation that has to be effected.

Assuming that the evaporator carries the density of the liquor from 40 per cent. solids up to say 80 or 90 per cent. solids, then the amount of work to be done in the evaporator is only 60 per cent. or so of the evaporation, and owing to the density of the liquor, bubbles of steam rise very reluctantly from the heating surface. In cases where substances of this nature have to be concentrated, it is essential that the circulation be as rapid as possible.

After studying this whole problem in very great detail, and carrying out a very enormous series of experiments, Mr. Kestner designed and patented a method of concentrating this liquor, which has been a very great success. The first thing Mr. Kestner set himself to prove was the actual

effect of temperature upon substances such as tannin extracts that are sensitive to heat, and he found that providing the time contact was short enough, there was in the majority of cases no limit within reason to the temperature. The ordinary film was too slow for this purpose, even though the speed of the vapors was in the neighborhood of 1 mile a minute, which is actually the speed obtained in the normal climbing film evaporator.

The liquor before entering the evaporator is brought up to near its boiling point, so that the moment it enters the climbing film tube evaporation takes place, and the film action begins. The liquor is carried up the climbing film tubes, it descends down the falling film tubes, returns up the climbing film, and finally goes down the falling film tubes into the separator at the bottom. The vapor passes to atmosphere, and the liquor is discharged from the bottom of the separator. It is mobile simply because of its temperature, and as soon as it cools it becomes solid. There have been hundreds of tons of extract made with this apparatus, and on test it has been shown that it has given results, when working in this way without a vacuum, equal to and in many cases better than those obtained with the vacuum type apparatus.

When extract is shipped from abroad this is the best method of shipping it. Usually moulds of a given size are used for the liquor to run into, and as soon as they are full they are stood on one side to cool, and the solid extract is then turned out from the moulds ready for transportation.

In some instances, the solid extract is sold in what is known as crystals, and in such cases it is dried in a rotary drier. This type of drier is arranged with a central drum, which is steam-heated. The drum runs in a bath of freshly concentrated extract, which is carried in a film on the surface. As the drum is revolving at a slow speed on a vacuum, the material dries on the drum, and is scraped, therefrom, at a point just before the drum goes back into the liquor again. These crystals are collected from the bottom of the case periodically.

Very often tanners buy solid extract from abroad which they wish to decolorize. For this purpose a number of plants have been put in, and are working with success. G. W. S.

Journal of the

American Leather Chemists Association

Vol. XIV OCTOBER, 1919 No. 10

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Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $6.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized July 16, 1918.

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VALUATION OF PYROXYLIN SOLVENTS AND LEATHER SOLUTION.

By Joseph R. Lorenz.

I. Industrial Application.

The recent years have witnessed the gradual development of the pyroxylin-coated leather industry. The latter has now become an enterprise of some importance. While, in a limited sense, its application may be regarded as a branch of currying, or leather-finishing, yet it must be said to enjoy a class by itself. Due proof of this is found in the related industry for the manufacture of imitation leather, in which the success of the process depends mainly upon the finish of pyroxylin which the canvas-duck base receives.

The use of pyroxylin preparations for the purposes mentioned dates back to the introduction of "patent leather" in the markets. Its object here was to increase the market value of already high-grade skins. However, a certain class of patent leather is now made in which linseed and other oils form the chief component of the varnish, and pyroxylin plays but a minor part. Aside from this, the commercial importance of pyroxylin is founded on a basis of true economy.

Pyroxylin is an economic adjunct to the leather and allied industries because it furnishes a means of reducing the present high cost of leather. This is especially true in the case of automobile and upholstery leathers. The great modern demand for

goods of this class has stimulated the pyroxylin industry to a marked extent. The manufacture of imitation leather has already been mentioned. In the application of pyroxylin to natural leather, the "flesh split" is employed, *i. e.*, that side of the split hide which is nearest the animal. Formerly, in producing high-grade shoe uppers other than calfskins, where the thickness of the skin made splitting advisable, the "grain split" only was used for shoe uppers, the "flesh split" being rendered marketable at a low figure by the application of a wax finish. If, now, in place of the wax finish, the "flesh split" is coated with a pyroxylin composition and embossed with an artificial grain simulating the natural, the resulting article—while not so valuable as a natural "grain split"—can be marketed more readily, and more profitably, than a wax-finished split.

The writer was connected for some time in the past with a large concern devoted exclusively to the production of pyroxylin-coated leather. While in this connection, he has had opportunity to study many of the methods in use for the valuation and analysis of pyroxylin or soluble cotton solutions and solvents. It may be stated at the outset that—so far as the writer has been able to determine—but little work on this subject has been published in the past; most of the literature examined gave a very meagre information on the specific question of analytical procedure. The scant attention accorded this question in the past may doubtless be attributed to the comparatively recent introduction, and to the heretofore undeveloped state of the pyroxylin-leather industry. With the possible exception of the methods of analysis and specifications formulated by the Federal Bureau of Standards for "airplane dope" preparations—mainly limited to acetyl cellulose derivatives and solvents,—there is a decided lack of uniformity in the methods of testing pyroxylin compounds commonly employed by the different analysts. Hence, the usual failure to obtain results in agreement with various collaborators is easily explained.

In order to correct to some extent the deficiencies noted above, and to collect the scattered data on methods of examination—including some modifications of methods for proximate analysis which the writer has found reliable and practical,—the following resumé of the subject is presented here for the possible benefit of

those whose interest is bound in this phase of the leather industry.

The importance of the analytical valuation of pyroxylin preparations can be readily appreciated by those who are in position to know the cost of the materials entering into such preparations. The solvents used are especially costly, so much so that the success of the industry depends in great measure on economy in the use of the necessary solvents.

2. Constituents of Commercial Leather Solutions, or "Dopes."

Solvents:

Amyl acetate
Ethyl acetate
Methyl-ethyl ketone
"Acetone oils"
Benzene
"Solvent Naphtha"
Camphor oil
"Fusel Oil"
Benzine
Methyl and ethyl alcohols

The first four are nitrocellulose solvents, the remainder oil and resin solvents.

Solids:

Soluble nitrocellulose
Oxidized ("Blown") oils
Pigment
Varnish gums (resins) - (rarely present).

3. Methods of Analysis.

On account of the varying composition of the fusel oil and amyl acetate used in a commercial pyroxylin resin lacquer, an accurate analysis of the latter is usually out of the question. The following scheme will be found sufficiently satisfactory where the examination is confined to the three solid constituents, resin, pyroxylin and pigment, and to the four liquids, amyl acetate, amyl alcohol (fusel oil), methyl alcohol and benzine:[1]

Amyl Acetate.—100 cc. of the varnish are placed in an Erlenmeyer flask, and 200 cc. of fusel oil added gradually and with constant stirring. The nitrocellulose precipitates and accumulates at the bottom in a voluminous gelatinous mass. Fifty cubic centimeters of the clear supernatent liquor are pipetted off and

[1] La Revue des Produits Chimiques, *Coll.*, 526, p. 119.

saponified with an excess of alcoholic potassium hydroxide. The amount of amyl acetate so obtained is multiplied by six to obtain the percentage in the original varnish.

Resins.— The liquid as well as the precipitate remaining from the preceding determination are poured upon a tared filter and washed with warm fusel oil until the latter extracts no more solids. After partial evaporation the filtrate is made up to 250 cc. with fusel oil, and 150 cc. evaporated to dryness in a weighed basin. The weight of residue obtained multiplied by two gives the percentage in the original varnish. The nature of the gum resins and camphor which constitute the residue may be determined by the usual methods.

Nitrocellulose (Pyroxylin).—The remaining precipitate on the filter paper is washed with a mixture of equal parts of acetone and amyl acetate, which dissolves the nitrocellulose. The filtrate is evaporated to dryness in a tared dish, and the latter then weighed. The weight in grams of residue obtained is equal to the percentage of nitrocellulose in the original varnish.

Pigment.—The residue remaining on the weighed filter paper after washing with amyl acetate and acetone consists of the pigment. It is dried at 100° C., and its weight gives the percentage of pigment in the original varnish.

Benzine.—50 cc. of the original sample are placed in a graduated cylinder, and 75 cc. of concentrated sulphuric acid added. The mixture is stirred vigorously and then allowed to stand for several hours. The benzine forms a layer at the top, either colorless or slightly tinted. Each cubic centimeter of this represents 2 per cent. benzine.

Methyl and Amyl Alcohols.—100 cc. of the original sample are distilled in a fractionating column. Below 75° C., each cubic centimeter corresponds to 1 per cent. in volume of methyl alcohol. The amyl alcohol is found by difference.

This method of fractionating can be extended to separating the different volatile constituents of the varnish.

Determination of Free Acid in Nitrocellulose Solvents and Solutions.—Free acid is normally absent in freshly prepared solvents and nitrocellulose solutions. Under the influence of light and moisture—especially the latter,—however, free acid soon de-

velops and increases in substance with age. While for leather-coating purposes the question of acid in the amounts ordinarily present in pyroxylin mixtures may possess little importance so far as influencing the quality of the coated stock, it is nevertheless desirable to keep the amount under control, and so check a source of possible potential mischief.

The following method proposed by A. D. Conley[2] is based upon the titration of the water extract of the solvent or solution under examination. In the case of amyl acetate, one volume is agitated in a separatory funnel with ten volumes of hot, freshly distilled water, and the liquids are allowed to separate and the aqueous layer titrated as soon as sufficiently cool, against tenth normal alkali, using phenolphthalein as indicator. In the case of nitrocellulose solutions, 10 or 12 grams are shaken with 100 cc. to 150 cc. of water, and the mass poured on a filter. The material on the filter is then washed twice with about 50 cc. of water, and the combined filtrate and washings titrated as above. According to some specifications, a nitrocellulose solution should not exceed 0.05 per cent. acid, as acetic. Some of the acid may be derived from the decomposition of the nitrocellulose, but it is convenient to calculate the whole to acetic acid. Care must be taken to secure water as free as possible from CO_2; the titration must be made very rapidly, as there is enough amyl acetate dissolved in the separated water to be saponified by the alkali, and the first red color must be taken as the end-point for this reason.

3—A. Separation of Volatile and Non-volatile Constituents of Nitrocellulose Solutions.

For the purpose of examining the volatile solvents and thinners of a prepared nitrocellulose solution, ordinary steam distillation may be employed for their recovery. The most expedient method is that of A. D. Conley,[3] in which the sample is heated in a paraffin bath to 120° C., until the low boiling solvents have passed over, when the distillation is continued with steam (by simply pouring water into flask containing the sample) until no further yield is obtained. The distillate with water is separated and dried. The separated water is again distilled to recover dissolved

[2] *Jour. Ind. Eng. Chem.*, October, 1915.
[3] *Loc. Cit.*

solvents. Traces of dissolved amyl acetate and fusel oil may be recovered by saturating the water with potassium carbonate.

3—B. Valuation of Nitrocellulose Solvents.

Amyl Acetate.—The commercial acetate is prepared from fusel oil and "grey" acetate of lime. It consists of a mixture of the acetates of the lower, as well as of the higher alcohols of the aliphatic series, and usually has a range of boiling points from 80° C., to 145° C.

The quality of a specimen of amyl acetate under examination is best determined for commercial purposes by distilling 100 cc. in a 250 cc. Erlenmeyer flask containing some pumice stone and connected to a Liebig condenser by means of a fractionating column.[4] The distillate is collected in a 100 cc. cylindrical graduate, and its volume read off at an interval of every 5° C. or 10° C. during the fractionation. The higher the yield of high-boiling fractions (from 125° C. to 140° C.) the purer is the sample in point of amyl acetate content, and the more pronounced are its solvent properties for nitrocellulose.

Should there be any doubt as to the identity of the high boiling fraction, the amyl acetate present in the former may be quantitatively determined, as follows: 5 grams of the fraction are weighed off by difference and dissolved in 20 cc. of neutral ethyl alcohol. An excess (50 cc. of a normal solution) of standard alcoholic potassium hydroxide solution is then added, and the mixture heated in a pressure flask on a water-bath to 80° C., or 90° C., for 30 minutes, the flask being occasionally rotated. The flask is cooled to room temperature, opened, a drop of phenolphthalein solution added, and the contents washed into a graduated flask with neutral alcohol and made up to 100 cc. Twenty cubic centimeters of the latter are withdrawn by means of a pipette ,placed in a small Erlenmeyer flask and titrated with standard acid to neutrality. The difference between the amount of alkali originally used and that neutralized by the standard acid is that combined with the acetic acid. Each gram of potassium hydroxide so used represents 1.070 grams of acetic acid, equivalent to 2.319 grams of amyl acetate.

[4] The writer employs a 4-bulb LeBel-Henninger Column.

$$\frac{5 \text{ Cc. normal KOH (combined)} \times 0.13012 \times 100}{\text{Weight of sample taken}} = \text{Per cent., amyl acetate}$$

in the fraction taken.

The ratio of amyl acetates to lower acetates found in the commercial article varies approximately as the ratio of amyl alcohols to foreign alcohols present in the fusel oil. The accompanying table taken in connection with the fractional distillation data obtained as above, will assist in identifying the source of the fusel oil from which the sample of acetate was derived.

Ethyl Acetate.—The incorporation of low boiling solvents (*viz.*, ethyl acetate) in a pyroxylin leather solution is an advantage insofar that less time is required in the drying of the coated leather, while at the same time a tougher film is obtained. A common drawback of most low boiling solvents is their hygroscopicity, or capacity for absorbing water, which definitely limits their usefulness in connection with pyroxylin lacquers. The presence of even traces of water in pyroxylin lacquer may cause the precipitation of the cotton on the surface of the coated leather in a manner known as "blushing." Commercial ethyl acetate usually also contains some free acetic acid formed by the hydrolytic action of the absorbed moisture. While not considered harmful in leather lacquers, the presence of traces of free acid in metal lacquers is highly objectionable.

In addition to the fractional distillation test, it is, therefore, advisable to test samples of ethyl acetate for dissolved water and free acid. Dissolved water may be estimated by adding to a measured volume of the specimen contained in a stoppered graduated cylinder, two volumes of benzene or toluene. After shaking for five minutes, the mixture is allowed to settle. The aqueous layer, if any, will be found at the bottom; its volume is expressed in percentage of water present in the original sample.

Commercial ethyl acetate boils from 69° C., to 85° C. The yield of low boiling fractions obtained is a measure of the purity of the sample.

Methyl-ethyl Ketone ("Acetone Oils)."—As a solvent for nitrocellulose, methyl-ethyl ketone is equal—if not superior—to amyl acetate. It is capable of dissolving a greater range of fatty and resinous substances than any other known solvent. A solution of nitrocellulose in methyl-ethyl ketone of a given concentra-

Constituents of Commercial Grades of Fusel Oil and Amyl Acetate.

Constituents[5]	Boiling points °C.	Fusel oil from rye[9]		Fusel oils from potatoes					Fusel oil from corn[14]	Boiling points of corresponding acetates °C.
				10		11	12	13		
		Crude	Free from water and ethyl alcohol	Crude	Free from water and ethyl alcohol					
Ethyl alcohol	78	4.02 %	—	2.76 %	—	—	—	4.89 %	—	77
Iso propyl alcohol	83	—	—	—	—	15.0 %	—	—	—	91
Normal propyl alcohol	97	3.17	3.69	5.87	6.854 %	3.0	2.7 %	0.08	3.69 %	101
Iso butyl alcohol	108	13.53	15.76	20.85	24.35	5.0	9.8	0.42	15.76	116
Normal butyl alcohol	117	—	—	—	—	6.5	—	—	—	124
Iso butyl carbinol[6]	131	68.53	79.85	58.88	68.76	27.5	87.4	94.24	75.85	140
Secondary butyl carbinol[7]	128									—
Iso propyl methyl carbinol[8]	112	—	—	—	—	6.0	—	—	—	125
Normal propyl methyl carbinol[8]	118	—	—	—	—	—	—	—	—	133
Normal amyl alcohol[8]	137	—	—	—	—	—	—	—	—	148
Hexyl alcohol	157	0.114	0.133	—	—	—	Trace	0.02	0.13	170
Water	—	10.15	—	11.61	—	12.5	—	—	—	—
Free fatty acids	—	0.137	0.160	0.009	0.011	—	—	—	—	—
Fatty acid esters	—	0.262	0.305	0.017	0.020	—	—	—	—	—
Furfurol	—	0.018	0.021	0.004	0.005	—	Trace	—	—	—
Terpene	—	0.028	0.033	—	—	—	—	—	—	—
Terpene hydrate	—	0.041	0.048	—	—	—	—	—	—	—
Boiling above 132° and retaining amyl alcohol	—	—	—	—	—	17.0	—	—	—	—
Ethyl alcohol, aldehydes and ethyl acetate	—	—	—	—	—	7.5	—	—	—	—
Total	—	100.000	100.000	100.000	100.000	100.00	99.9	99.65	95.43	—

[5] Normal constituents listed in order of boiling points.
[6] Iso amyl alcohol-chief component of fermentation amyl alcohol.
[7] Active L-amyl alcohol-present in fermentation amyl alcohol from 13 to 58 per cent.
[8] Three amyl alcohols grouped here do not occur ready-formed in fermentation fusel oil.
[9] Karl Windisch. Ber. Polytech. Inst.
[10] Karl Windisch. Ber. Polytech. Inst.
[11] Rabuteau. *Bull. Soc. Chim.*, 1886, 45, 333.
[12] Rüdakoff and Alexandroff. *Chem. Zeit.*, 1904, 28, 187.
[13] Kruis and Rayman (Worden's "Nitrocellulose Industry" 1).
[14] Le Bel. *Bull. Soc. Chim.*, 1879, 31, 104.

tion is less viscous than a corresponding solution in amyl acetate. In addition, methyl-ethyl ketone boils at a medium temperature (81° C.). These qualities would seem to answer in the main the requirements of an ideal pyroxylin lacquer constituent.

In common with ethyl acetate, and to a more marked extent, methyl-ethyl ketone and other low boiling ketones show a great affinity for water. For this reason they can, unfortunately, be used but sparingly in leather finishing compositions.

Methyl-ethyl ketone is chiefly employed as an accelerating and "harmonizing" agent. By its means a perfect solution is often effected of an otherwise refractory formula, whose antagonistic tendencies are usually due to the introduction of too much benzine. For this purpose, a little goes a long ways. The undesirable property of the ketones, *viz.*, their hygroscopicity, may be largely overcome by the use of fusel oil in admixture. Their solvent value for nitrocellulose is not impaired in this manner, though in practice the usefulness of such a mixture would necessarily be limited owing to the difference in the boiling points of ketone and fusel oil.

Commercial methyl-ethyl ketone is also known as "Light Acetone Oil." A second class of mixed ketones—known as the "Heavy Acetone Oils"— boils from 80° C., to 200° C. While the former is an excellent solvent for nitrocellulose, the high boiling article is practically valueless as a nitrocellulose solvent.

The usual tests applied in practice include fractional distillation, water-absorbtive capacity, and estimation of dissolved water. The water-absorptive capacity is a measure of the solvent value of a particular specimen of ketone for nitrocellulose, since it fixes the proportion of low-boiling ketones present in the sample. Conversely, the proportion of higher ketones of little or no solvent action is indicated by the volume of the residual layer. The test is readily made by agitating 50 cc. of the sample with 50 cc. of water in a stoppered graduated cylinder. The increase in volume of the ketone layer is taken as the water-absorbtive index.

The determination of the quantity of dissolved (hygroscopic or added) water in specimens of methyl-ethyl ketone is best made by means of the benzene method. The latter will be found outlined above, under "Ethyl Acetate."

3—C. Valuation of Nitrocellulose Nonsolvents.

Benzene and "Solvent Naphtha."—The coal-tar distillates, benzene and its homologues, are excellent solvents for oxidized ("blown") oils, rubber, resins, etc. Because of their stable character, their non-hygroscopicity and low cost, they are extensively used as diluents or "thinners" of pyroxylin-leather lacquers. For this purpose, the coal-tar distillates in general may be used much more freely than petroleum benzine without causing the precipitation of the dissolved cotton. The choice of the several members of the benzene series for use as thinners depends on the rate of evaporation desired, which may be controlled at will.

As a constituent of pyroxylin solutions, so-called "water-white benzene"—the purest of commercial grades—is universally used. This grade of benzene distils completely between 80° C., and 82° C.

"Solvent Naphtha" consists of a mixture of the high boiling members of the cyclic series, xylene (boiling point, 140° C.), cumene (boiling point, 151° C.), mesitylene (boiling point, 163° C.), pseudocumene (boiling point, 169° C.) etc., in varying proportions.

In practice it has been found that the highest boiling members of the series in question exhibit a wider range of solubilities, and show more pronounced solvent tendencies for oxidized oils, resins and gums, than do the low boiling members; in an analogous manner, this also holds true for members of the petroleum series. For this reason, and because it possesses a gradation of boiling points and corresponding rates of evaporation, solvent naphtha finds more extensive application as a lacquer thinner than does any single, or low boiling member of the cyclic series.

As in the case of other volatile liquids, fractional distillation affords the simplest and most useful means for determining the quality of specimens of coal tar distillates to be used as pyroxylin thinners. A source of danger in the use of solvent naphtha for thinner purposes arises in the probable presence of naphthalene in the poorly-refined article. Naphthalene is scarcely compatible with the *bona fide* solids present in pyroxylin oil lacquers, causing stains in, and rendering brittle the film on the surface of the coated leather. The test for naphthalene may be made by cooling

to room temperature the flask containing the oily residue remaining upon distillation of the sample of solvent naphtha. In the presence of naphthalene, the oily residue will solidify to a crystalline mass.

Camphor Oil.—Japanese camphor oil occurs together with camphor in the tree *Laurus Camphora,* and is obtained by distillation of the trunk, leaves or roots. From the semi-solid mixture of camphor and oil, the crude product is obtained by pressing. The crude oil still contains from 20 to 30 per cent. of solid camphor, which is recovered by fractional distillation. In a strict sense, camphor oil must be regarded as a by-product in the manufacture of camphor and safrol.

For commercial purposes, the rectified oil is separated into two fractions, the one containing the low boiling (from 160° C., to 200° C.), and the other the high boiling (from 200° C., to 300° C.) members of the terpene series; these are known respectively as "light camphor oil" and "heavy camphor oil." Both fractions consist of complex mixtures of terpenes and camphor bodies. For pyroxylin thinner purposes, "light camphor oil" is generally preferred, since its rate of evaporation more nearly accords with that of commercial solvent naphtha.

Camphor oil is invariably incorporated in a pyroxylin oil lacquer thinned with solvent naphtha. Though normally a nonsolvent of nitrocellulose, its presence in a pyroxylin lacquer tends to prevent precipitation of the cellulose in the drying film during the period of volatilization of the solvent naphtha, after the last of the lower-boiling *bona fide* solvent,—amyl acetate,—has been driven off. Thus, the function of camphor oil as described is somewhat analogous to that of solid camphor incorporated in a celluloid mixture. It is a familiar fact that camphor exerts a "latent" solvent action upon dry nitrated cotton as soon as a sufficiently elevated temperature is attained. However, even granting the presence of a certain quantity (which is usually small) of dissolved camphor in the camphor oil employed as pyroxylin thinner, the conditions of drying temperature, composition of film, etc., are so radically different in the case of leather enameling, that no true "latent" solvent action,—such as forms the basis of celluloid manufacture,—can be held to take place. The probable explanation of the observed effect of camphor oil on the drying film is

that—under the conditions of such drying—camphor oil has a sufficiently great affinity for nitrocellulose to keep the latter in a dissolved state until the last of the liquids are volatilized.

For purposes of evaluation, main reliance is placed on the fractional distillation test. Light camphor oil boils from 165° C., to 190° C., the largest fraction (30-40 per cent.), distilling at 170° C. The odor of the several fractions should be noted as roughly indicating the extent of camphor or safrol remaining in the sample under examination. The specific gravity ranges from 0.870 to 0.910. That of "heavy" camphor oil (which usually contains much safrol) varies from 0.960 to 1.000.

The estimation of camphor in camphor oil may be made in the following manner:[15] At least 300 grams of the oil are fractionated, the distillates below 195° C., and those between 195° C., and 220° C., and above 220° C., being collected separately. The second fraction, which contains the whole of the camphor, is kept in a freezing mixture for one hour, when the camphor is filtered off, wrapped in filter cloth and then in filter paper, and pressed for one-half hour. The cake of camphor thus obtained is wrapped in fresh filter paper and again pressed for 15 minutes, and is then weighed. The mother-liquor from which the camphor was previously separated is next redistilled, and the fraction at 205° C., to 220° C., frozen and treated as above. Five distillations are necessary to obtain all the camphor from the original fraction containing it.

Fusel Oil.—Fusel oil is occasionally used in the vehicle portion of pyroxylin solutions. Its presence, however, is commonly associated with that of petroleum benzine, and hence usually indicates an inferior or cheap mixture. It is a well known fact that petroleum benzine is decidedly antagonistic to the majority of the solvents met with in nitrocellulose solutions, especially those containing considerable quantities of methyl or ethyl alcohol. In order to make it possible to introduce benzine into the solvent mixture for cheapening purposes, fusel oil is added to render the whole miscible. In the presence of a small quantity of fusel oil, methyl or ethyl alcohol becomes miscible with petroleum benzine in all proportions.

[15] H. Löhr, *Chem. Zeit.*, 25, 292, (1901).

Fusel oil is, however, legitimately employed in instances where it is desired to counteract the hygroscopicity of solvent mixtures containing large proportions of alcohol, ketones, or ethyl acetate. Its employment in this connection has been discussed under "methyl-ethyl ketones."

In the examination of a specimen of fusel oil, ordinary fractional distillation furnishes valuable information as to the quality of the sample. In the table of "Constituents of Commercial Grades of Fusel Oil and Amyl Acetate," shown elsewhere in these pages, the average compositions of fusel oils derived from the fermentation of potatoes, rye and corn are given.

The presence of lower alcohols (chiefly ethyl alcohol) in commercial fusel oils may be detected and the quantity estimated by means of the calcium-chloride test. This test is made by agitating 25 cc. of the sample contained in a 50 cc. stoppered graduated cylinder with 25 cc. of a saturated aqueous solution of calcium chloride. The increase in volume of the calcium-chloride layer multiplied by four gives the percentage of lower alcohols present in the original sample.

Benzine.—The application of petroleum benzine to solvent mixtures employed as thinners of pyroxylin compositions has already been discussed under "Fusel Oil." It is hardly necessary to add here that petroleum benzine is never found in high-grade pyroxylin leather solutions. Its presence in such solutions must always be regarded as evidence of adulteration and of inferiority. As has been previously stated, the quantity of petroleum benzine which may be incorporated in a pyroxylin-oil lacquer without causing precipitation of the dissolved nitrocellulose is limited; as a rule, it cannot be used nearly as freely as is permissible with members of the coal-tar family, *i. e.*, benzene and its homologues.

Unfortunately, it is often a difficult—in some cases an impossible—matter to arrive at an estimation of the amount of petroleum benzine which has been added to a solvent mixture containing the usual variety of alcohols, ketones, esters, terpenes and coal-tar distillates. In the absence of the latter (which is seldom the case,) however, the sulphuric-acid-polymerization test affords a simple and convenient means for determining the proportion of petroleum benzine present in a sample of mixed solvents. The writer has found the method in question sufficiently

accurate for practical purposes. The test may be carried out by treating 35 cc. of the sample of solvent under examination contained in a 100 cc. graduated cylinder, with 55 cc. (or one and one-half volumes) of strong sulphuric acid. The acid is added in small portions with constant stirring, the mixture being cooled under the tap after each such addition. After stirring for several minutes, the mixture is allowed to come to room temperature. The volume of unpolymerized upper layer is then read off, and the result expressed in percentage of petroleum hydrocarbons present in the original sample. In the simultaneous presence of coal-tar distillates, the above test yields erratic results. This is explained by the fact that the sulphonation of benzene and its homologues is never complete except under prolonged treatment with a large excess of acid at elevated temperatures. Under the conditions of the above test, in experimenting with commercial solvent mixtures containing known quantities of coal-tar distillates, the writer has found the sulphonation of these bodies to proceed to the extent of 60 to 80 per cent., depending on the relative proportion of distillates to sulphuric acid employed.

Methyl and Ethyl Alcohols.—Methyl and ethyl alcohols—more especially the first—are sometimes employed in pyroxylin solvent mixtures when it is desired to increase the rate of evaporation of the drying film. Their utility in this connection is, however, limited in view of the marked hygroscopicity of these substances. This objectionable feature is further enhanced as a result of the rapid volatilization of methyl and ethyl alcohols, which induces the condensation of moisture at a correspondingly increased rate.

Pure methyl or ethyl alcohol is incapable of dissolving nitrocellulose. In admixture with ethyl ether, however, a nitrocellulose solvent is obtained which is employed in large quantities in the commercial production of gun-cotton and of collodion.

The preference shown for methyl or "wood" alcohol for pyroxylin thinner purposes is explained by the fact that the commercial product always contains acetone, which accounts for the slight solvent tendency exhibited by the former body for nitrated cotton.

For proximate analysis, a sample of wood alcohol is usually submitted to fractional distillation. The pure alcohol distils over at 67° C. That portion which distils below 60° C., consists of

acetone, while that above 70° C.,—which ordinarily should not exceed 15 per cent.—contains water and other foreign bodies.

The valuation of a sample of commercial ethyl alcohol may be accomplished by simply determining the specific gravity at 15.5° C., by means of an accurately calibrated pycnometer. The alcoholic content is then found by reference to the tables contained in the United States Pharmacopoeia IX. In the case of denatured ethyl alcohol, the result may be low or high, depending on the nature and amount of denaturing agent present. For practical purposes, however, the error will not seriously affect the value of the result.

3—D. Valuation of Nitrocellulose Solutions and Lacquer Bases.

Nitrocellulose, or Soluble Cotton Content.—A large number of nitrocellulose non-solvents have been experimented with by different investigators in the hope of finding a suitable precipitant for nitrated cotton in solution. With the possible exception of chloroform, all may be discarded as valueless for quantitative work. Chloroform itself must be used under carefully regulated conditions in order to yield results that may be relied upon in general practice.

The writer has sought to determine the conditions best adapted to the quantitative estimation of nitrocellulose by means of chloroform; on the basis of those found, the following analytical method has been compiled.

The use of chloroform in pyroxylin analyses was originally suggested by A. D. Conley,[16] who proposes taking a measured volume of the sample of cotton solution for analysis. This procedure is open to objection however, since with a heavy, viscous liquid of this nature a pipette cannot be employed, and no high degree of accuracy can be expected from the use of an ordinary graduate. Instead of a measured volume, the writer prefers to take an accurately weighed portion of the sample; the volume corresponding to this is then calculated on the basis of the specific gravity of the solution. The specific gravity required may be determined in a simple manner and with sufficient accuracy by means of a 25 cc. cylindrical graduate.

[16] *Loc Cit.*

The writer's method is as follows: 5 to 8 grams (of 12 ounce solutions—less of heavier solutions) are weighed off by difference into a 250 cc. Soxhlet flask and dissolved in 30 cc. of amyl acetate. To the resulting solution 50 cc. of chloroform delivered from a graduated cylinder ***are added in small successive portions, with rapid and constant stirring.*** After standing for some time, the liquid in the flask is filtered through a 15 cm. paper contained in a 4-inch covered funnel. The bulk of the precipitate is then transferred to the paper by means of a spatula kept saturated with chloroform. After the greater part of the supernatent liquid has drained off, the filtrate is tested with 10 cc. or 15 cc. of chloroform to determine whether complete precipitation has been effected. Should the filtrate yield a further precipitate, enough chloroform is added to throw out the remainder of the dissolved cotton, and the second precipitate added to the first in the funnel. The filtrate should be tested again to make certain that no cotton remains in solution.

The precipitate adhering to the walls of the flask is washed with chloroform, and the washings rinsed over the main precipitate in the funnel. The contents of the funnel are now washed three or four times with chloroform, the paper being filled to the brim each time. After draining completely, a tared, flat-bottomed, glass crystallizing dish is placed under stem of funnel; the precipitate in the paper is now dissolved in a 1 : 1 mixture of redistilled amyl acetate and acetone. The latter is best delivered from a small wash-bottle, which is subsequently used to dissolve any precipitate remaining in the flask. The latter is rinsed into the funnel, the whole being allowed to filter into the glass dish placed beneath. Paper and funnel are finally rinsed with solvent, the dish placed in a hot-air drying oven (temperature not to exceed 110° C.) and allowed to remain over night. When no further smell of the solvent can be detected, the dish is transferred to a desiccator, cooled and weighed.

(NOTES: Above determination is best made in duplicate. For absolute results, the weight of cotton residue found in the above manner must be corrected for non-volatile matter preseht in the quantity of amyl-acetate-acetone mixture required to dissolve the precipitated cotton.)

Specific Gravity.—A dry 25 cc. cylindrical graduate is tared (to two decimal places), filled with distilled water at 20° C., and

reweighed. Difference in weight represents the water equivalent. The graduate is emptied, dried with alcohol and ether, filled to the mark with the sample of cotton solution, covered with a small beaker and allowed to stand until air bubbles have escaped. When the meniscus has been established, it is reweighed.

$$\frac{\text{Weight of sample}}{\text{Water equivalent}} = \text{Specific gravity}$$

$$\frac{\text{Grams cotton residue} \times 133.51 \times \text{specific gravity}}{\text{Weight of sample taken}} = \text{Cotton content, in}$$

ounces per gallon.

Chloroform Recovery.—The filtrate received in the preceding determination (consisting of chloroform in admixture with some amyl acetate) is transferred to a 500 cc. Erlenmeyer flask, some pumice stone added, and the flask connected to a Liebig condenser and fractionating column. The mixture is distilled over a low flame until the temperature reaches 75° C., or 80° C., the distillate being collected in a 500 cc. separatory funnel. The latter is permitted to stand over night, when the small quantity of water carried over with the distillate will be found to have collected in drops on the surface, from which the lower chloroform layer may be drained off.

Oxidized ("Blown" or "Processed") Oils.—So-called "blown" oils employed in connection with soluble cotton as the basis of pyroxylin leather solutions, are second in importance only to soluble cotton itself. Blown oils chiefly used are rape-seed, soybean and castor. Linseed-oil when used is sometimes "blown," but the "boiled" oil is more commonly employed. The object sought for in the blowing operation is the same as that attained in the "boiling" process,—namely, increased rate of drying or hardening of the oil so treated. The difference between the two operations lies in the means taken to accomplish this end, which, in turn, is reflected by a difference in the nature of the end-products formed. Whereas "boiling" induces polymerization or condensation, and but little oxidation in the oil so treated, "blowing" is primarily an oxidation process.

"Blown" oils are produced by the action of air currents upon oils of the drying or semi-drying variety, at slightly elevated temperatures. In effect, "blowing" increases the saturated fatty acid content of the oil. The iodine number progressively dimin-

ishes as the unsaturated fatty acids disappear, and by its means the progress of the reaction may be accurately followed.

"Blown" oils are characterized by a heavy, viscous body, light color, transparency and bland smell (the latter denoting the absence of fatty decomposition products, principally acrolein). "Boiled" oils are usually darker-colored products, with the characteristic penetrating odor of acrolein commonly in evidence.

A specimen of "blown" oil suitable for leather enamelling purposes should show an iodine number of between 60 and 70.

Pigments.—The pigment incorporated in a pyroxylin-oil leather lacquer is usually some form of finely-divided carbon, such as lampblack. Colored pigments in use are the common mineral earths employed as paint bases. The introduction of pigment into pyroxylin-leather lacquers is effected by the usual process of grinding in the oil-base in an ordinary paint mill.

Methods for the physical valuation of specimens of carbon pigments, such as covering power, fineness of granules, and—in the case of metallic-earth pigments, chemical composition, may be had by reference to any of the standard works on paint analysis.

Varnish Gums (Resins).—The softer varieties of gums and resins are occasionally though infrequently employed in connection with the oil-base which, combined with pigment, dissolved nitrocellulose and volatile thinner, goes to form the ultimate product, pyroxylin-leather lacquer, or "dope." Pyroxylin lacquers containing gums exhibit the character of a modified varnish or enamel. Inasmuch, however, as the addition of gums or resins to preparations of this description causes the residual film on the leather to lose much of its desirable elasticity, with the resulting tendency to "craze" or crack, it is the usual practice to omit these bodies.

The chemical examination of specimens of gums and resins is confined chiefly to the acid value determination. Color, and solubility of the specimen in volatile liquids are also criterions on which to base the quality of the sample.

Conclusion.

The purpose of the foregoing has been to cover, in as complete a manner as was considered practicable, the series of raw materials composing the nitrocellulose-oil preparations used in the

upholstery and split-leather industries of the present day. The different components of the modern pyroxylin-leather lacquer have been considered individually from the analyst's standpoint, and collectively in their relation to the finished product of the industries referred to. It is realized that the list of materials presented could be augmented by including the numerous patent solvents and solvent-mixtures found on the market and in demand by certain manufacturers who prefer the "ready-mixed" preparations. However, for the sake of simplicity, and in order to avoid the duplication incident to a discussion of the properties of materials correlated by a common basis, the writer has confined himself to only such components as are "basically" present in the majority of commercial preparations of this description.

It should be borne in mind that the evaluation of these materials by the physical or chemical means at the disposal of the average industrial chemist is not capable of very extended accuracy. The very nature of these substances in most cases does not permit of other than a proximate analysis. Many of the methods in common use, notably that for the fractional distillation test, are largely empirical. The results which they yield depend on the particular "*modus operandi*" employed; hence, they are valuable merely in a relative sense.

On the other hand, the fact should not be overlooked that in practice it is usually unwise to attempt a high degree of accuracy in the analysis of colloid materials; the same applies with regard to going beyond the scope of examination prescribed for a certain material included in this category, in order to fix its status or commercial value. While, admittedly, for evaluation purposes a precise analysis is to be preferred, in practice an extended examination often entails a loss of time without either narrowing the limits of error, or yielding additional information of direct benefit.

In conclusion it may be stated that an intelligent application of the methods at present available—however imperfect—to the economic control of the works' operations concerned in the production of upholstery, split ana patent leathers, cannot fail to yield gratifying results of practical benefit to the manufacturer.

ANALYSES OF DIFFERENT TANNAGES OF STRAP, HARNESS AND SIDE LEATHER.*

By L. M. Whitmore.

During the period when the Government was purchasing leather in large quantities, a great number of samples of different types of leathers were analyzed at the Bureau of Standards. The greater part of this work was done for the Inspection Division of the Ordnance Department and the Division of Purchase and Supply of the Quartermaster Corps. As the analyses made covered a great many types and tannages of leather, it was thought that the members of the A. L. C. A. might be interested in the data secured.

The data show the variation that may be expected between different tannages of the same type of leather, the variation that occurs in the composition of a single tannage, and the average composition of the different types of leather. Much of the leather was tanned especially for Government use, and the composition of the leather may not correspond to that of the leather put out by the same tannery under normal conditions. The wide variation shown in some cases is due to changes in the process of manufacture instituted in order to have the leather comply with the Government specifications, and should not be considered as a normal variation. This is especially true in regard to the grease content of russet harness, as the specifications for grease in this type of leather were changed from the 9 to 12 per cent. called for in the original specifications of the Ordnance Department, to the 15 to 20 per cent. required by the final specifications adopted by both the Ordnance Department and the Quartermaster Corps.

The data given for the different tannages are sometimes based on the analysis of a large number of samples, and in some cases are the result of the analysis of a single sample. In cases where more than one sample was analyzed, the high, low and average results are given, together with the total number of samples analyzed. Where only one figure is given, it is the result of the analysis of a single sample of leather, and the data should be interpreted accordingly. In the case of the chrome-retan upper leathers, there are fewer analyses made, and all the available data

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are given. The averages given for chrome-retan leather are the average for all the samples analyzed, and not the average of the different tannages.

In calculating the average analyses of the other leathers, the average analyses of the different tannages are given equal weight, although the data on one tannage may be based on more analyses than the corresponding data on another tannage. As the petroleum ether extract and acid were the items that most frequently failed to come within specifications, the data for these determinations are based on more analyses than the data for hide substance, degree of tannage, etc.

The official methods of the A. L. C. A. were followed wherever possible, and the Proctor-Searle method was used in the determination of mineral acidity. The samples as prepared for analysis were a composite of samples cut from the back, butt and belly; and cuttings from several different sides often made one analytical sample. The average moisture content was about 10 per cent. and the data are all calculated on the basis of the air-dry sample.

The permissible errors in the determination of the different constituents of the leather are all quite small when compared with the errors involved in sampling and the preparation of the sample. In the analysis, the limits of error for the different determinations made on a sawed sample and based on the total amount present, are about as follows:

	Per cent.
Epsom salts	1
Ash	1
Hide substance	2
Petroleum ether extract	2
Water-solubles	3
Combined tannin	6
Degree of tannage	8
Acidity	10
Glucose	15

Considering these errors, we have not thought it advisable to report any of the determinations further than the third place. In the case of unsaponifiable material, acidity, glucose, combined tannin and degree of tannage, the results are sometimes given in three figures, although the third figure is not significant.

A careful consideration of the data given on the following pages will show that it is impossible to make leather specifications which require a very definite amount of stuffing, and have them complied with. A maximum or a minimum alone would be sufficient if a maximum were stated in the case of leathers sold by the pound, and a minimum in the case of leathers sold by the foot. Where both are given, they should be far enough apart to allow for incidental variations. If the specifications are to be adhered to, a difference of at least 5 per cent. should be allowed.

In the case of ash, water-soluble material, glucose, salts, and acidity, maxima can be set and can readily be complied with where the tannery is running with proper chemical control.

The figures for degree of tannage show large variations, which are probably partly due to permissible errors in analysis. A difference of 4° of tannage is quite possible from this cause alone. The greater part of the variation is probably due, however, to the actual tanning process. Any specifications for degree of tannage should have at least fifteen points between maximum and minimum to allow for the unavoidable variations in the product, and its sampling and analysis.

The data in the following tables were secured from samples analyzed at the Bureau of Standards between November 15, 1917, and November 15, 1918.

TABLE I.

ANALYSES OF BLACK HARNESS LEATHER.

Received by the Bureau of Standards, from November 15, 1917, to November 15, 1918.

Tannage	Total ash	Petroleum ether extract	Water soluble	Glucose	Hide substance	Combined tannin	Degree of tannage	Salts	Acidity	Unsaponifiable
A.....Max.	0.73	36.8	15.2	6.0	35.6	23.7	68	1.6	0.67	—
Min.	0.38	20.5	11.9	1.7	32.4	9.5	29	0.8	0.12	—
Av..	0.57	28.2	13.7	3.5	33.5	18.6	52	1.2	0.40	41
No. of Anal.	7	11	10	11	5	4	4	2	10	—
B.....Max.	0.44	40.2	11.4	1.7	32.1	19.7	67	—	0.76	—
Min.	0.37	30.7	9.9	0.2	28.6	17.7	55	—	0.18	—
Av..	0.41	34.1	11.0	0.7	30.3	18.7	62	—	0.36	55
No. of Anal.	4	7	4	6	2	2	2	—	6	—
C.......Av.	0.44	25.2	12.1	0.5	39.4	15.1	38	—	0.00	64

TABLE I.—(*Continued*)

Tannage	Total ash	Petroleum ether extract	Water soluble	Glucose	Hide substance	Combined tannin	Degree of tannage	Salts	Acidity	Unsaponifiable
D.....Max.	0.67	45.5	18.0	1.2	31.3	15.4	61	—	0.77	—
Min.	0.25	19.0	8.6	0.3	24.4	11.8	38	—	0.04	—
Av..	0.39	37.5	10.7	0.6	29.1	14.6	48	—	0.34	—
No. of Anal.	16	25	18	14	5	5	5	—	21	—
E.....Max.		38.5	19.0	9.4	—	—	—	—	0.50	—
Min.	0.99	34.5	18.6	6.0	—	—	—	—	0.13	—
Av..		35.8	18.8	7.3	—	—	—	—	0.35	29
No. of Anal.	—	6	2	5	—	—	—	—	4	—
F... ...Av.	0.26	25.1	14.1	2.9	35.2	16.6	47	—	—	46
G.....Max.	0.73	45.7	15.1	6.2	31.8	16.7	52	1.6	0.84	57
Min.	0.60	27.6	10.6	4.0	30.2	12.9	43	1.6	0.32	33
Av..	0.66	33.9	13.1	4.9	31.0	14.8	48	1.6	0.55	45
No. of Anal.	6	9	5	3	2	2	2	2	6	2
H.....Max.	0.70	19.6	20.1	6.8	—	—	—	—	0.62	—
Min.	0.62	15.9	11.4	3.3	36.3	19.9	55	1.9	0.51	—
Av..	0.66	17.7	15.7	5.1	—	—	—	—	0.56	28
No. of Anal.	2	2	2	2	—	—	—	—	2	—
I..... Max.	0.48	37.6	12.7	5.0	36.5	17.2	58	—	0.62	—
Min.	0.34	28.1	7.5	0.4	29.4	10.1	27	—	0.08	—
Av..	0.39	32.7	11.8	2.8	33.0	13.5	42	—	0.21	0.3
No. of Anal.	8	8	6	8	7	7	7	—	7	—
J..... Max.	0.29	30.6	18.5	4.9	—	—	—	—	0.19	—
Min.	0.20	25.4	12.2	0.4	35.6	12.6	35	—	0.00	—
Av..	0.25	28.0	15.3	2.8	—	—	—	—	0.09	—
No. of Anal.	2	2	2	2	—	—	—	—	2	—
K......Av.	1.01	20.8	9.2	2.9	—	—	—	—	—	8.0
L.....Max.	0.30	28.7	17.3	2.8	—	—	—	—	0.18	—
Min.	0.24	26.6	13.6	1.0	—	—	—	—	0.08	50.0
Av..	0.27	27.7	15.5	1.9	30.7	14.6	39	—	0.13	—
No. of Anal.	2	2	2	2	—	—	--	—	2	—
M......Av.	0.38	30.0	12.0	0.3	37.1	12.5	34	—	0.20	75
N...... Av.	0.28	33.6	10.5	0.6	33.0	15.7	48	—	0.54	—
O.......Av.	2.10	29.6	21.5	8.3	—	—	—	2.6	Barytes	1.6
P.......Av.	0.37	34.0	9.1	0.7	33.1	18.8	57	—	0.17	22
All Tannages Max.	2.10	45.7	21.5	8.3	39.4	23.7	68	5.1	0.84	75.0
Min.	0.20	15.9	7.5	0.3	24.4	9.5	27	0.8	0.00	0.3
Av..	0.60	29.3	13.7	3.0	33.7	15.6	46	2.7	0.31	47
No. of Anal.	54	78	57	59	28	27	27	6	63	12

TABLE II.

SUMMARY OF ANALYSES OF RUSSET HARNESS LEATHER.

Received by the Bureau of Standards from November 15, 1917, to November 15, 1918.

Tannage	Total ash	Petroleum ether extract	Water soluble	Glucose	Hide substance	Combined tannin	Degree of tannage	Acidity	Unsaponifiable
A .. .Max.	0.77	25.5	17.0	1.5	37.8	27.3	75	1.32	63
Min.	0.10	9.2	8.3	0.2	31.7	23.3	62	0.00	0.2
Av..	0.30	15.7	14.0	0.7	35.6	24.9	70	0.44	43
No. of Anal.	27	121	70	71	3	3	3	61	14
B.....Max.	0.58	24.6	12.4	0.72	44.2	25.7	62	1.20	27
Min.	0.12	8.7	9.0	0.30	36.2	20.8	57	0.20	0.7
Av..	0.42	14.6	11.0	0.44	39.9	23.7	59	0.61	11.4
No. of Anal.	12	36	28	9	3	3	3	35	5
C.....Max.	—	24.4	14.6	—	—	—	—	0.65	—
Min.	—	12.8	9.9	—	—	—	—	0.07	—
Av..	0.70	17.9	12.0	0.48	38.0	22.0	58	0.35	11
No. of Anal.	—	8	8	—	—	—	—	6	—
D.....Av..	0.30	26.8	10.3	0.2	36.0	17.2	48	0.23	—
E.... Max.	0.44	28.6	11.2	0.48	37.2	22.3	60	0.45	—
Min.	0.18	22.6	7.8	0.25	35.4	18.2	51	0.08	—
Av..	0.34	25.9	9.7	0.36	36.3	20.2	55	0.25	—
No. of Anal.	4	6	6	3	2	2	2	4	—
F ....Max.	0.42	22.0	16.1	5.0	—	—	—	0.75	61
Min.	0.16	7.0	11.5	0.2	—	—	—	0.14	33
Av..	0.29	14.2	14.0	1.0	—	—	—	0.30	37
No. of Anal.	14	74	31	67	—	—	—	20	4
G.....Max.	1.09	15.1	12.0	3.0	43.6	27.8	59	0.70	51
Min.	0.56	10.2	7.0	0.2	42.8	25.6	65	0.38	32
Av..	0.91	12.3	9.8	1.0	43.2	26.7	62	0.52	42
No. of Anal.	4	6	6	6	2	2	2	6	2
H ....Max.	—	17.1	19.5	—	—	—	—	0.24	—
Min.	—	11.9	13.1	—	—	—	—	0.00	—
Av..	—	14.3	14.2	0.44	—	—	—	0.09	—
No. of Anal.	—	6	4	—	—	—	—	5	—
I.....Max.	0.44	14.5	16.7	0.56	41.4	29.8	72	0.99	—
Min.	0.23	6.0	9.5	0.12	41.1	27.8	68	0.16	—
Av..	0.34	9.8	12.8	0.35	41.2	28.8	70	0.45	—
No. of Anal.	8	31	16	10	2	2	2	21	—

TABLE II.—(*Continued*)

Tannage	Tatal ash	Petroleum ether extract	Water soluble	Glucose	Hide substance	Combined tannin	Degree of tannage	Acidity	Unsaponifiable
J .... Max.	0.60	21.9	21.0	5.4	—	—	—	1.08	43
Min.	0.06	7.4	11.8	0.3	—	—	—	0.08	25
Av..	0.37	14.0	14.9	1.6	—	—	—	0.30	36
No. of Anal.	27	49	17	47	—	—	—	9	6
K .... Max.	0.33	17.8	13.6	3.7	43.1	26.6	66	1.20	—
Min.	0.12	7.2	9.5	0.2	40.5	26.3	61	0.33	26
Av..	0.20	13.1	10.9	0.8	41.8	26.4	63	0.79	—
No. of Anal.	6	12	7	7	2	2	2	12	—
L .....Max.	—	21.7	7.4	0.4	—	—	—	0.49	35
Min.	—	19.8	7.3	0.2	—	—	—	0.38	20
Av..	0.62	20.3	7.3	0.3	39.4	28.4	72	0.43	27
No. of Anal.	3	3	2	2	—	—	—	3	2
M .... Max.	0.50	18.4	13.2	1.0	—	—	—	0.77	—
Min.	0.42	9.5	7.3	0.3	—	—	—	0.18	—
Av..	0.45	13.7	11.2	0.6	—	—	—	0.38	30
No. of Anal.	5	16	10	12	—	—	—	12	—
All Tannages Max.	1.09	28.6	21.0	5.4	43.6	29.8	75	1.32	63
Min.	0.06	6.0	7.0	0.1	31.7	17.2	48	0.00	0.2
Av..	0.44	15.5	12.6	0.6	39.0	24.2	61	0.39	29
No. of Anal.	112	368	205	249	17	17	17	195	36

TABLE III.

SUMMARY OF ANALYSES OF RUSSET STRAP LEATHERS.

Received by the Bureau of Standards, from November 15, 1917, to November 15, 1918.

Tannage	Total ash	Petroleum ether extract	Water soluble	Glucose	Hide substance	Combined tannin	Degree of tannage	Acidity
A .... Max.	0.80	17.9	14.0	0.8	—	—	—	1.09
Min.	0.32	2.2	7.7	0.1	—	—	—	0.18
Av..	0.55	12.7	11.1	0.5	—	—	—	0.58
No. of Anal.	4	82	4	6	—	—	—	72
B .... Max.	—	16.6	12.4	0.9	—	—	—	1.34
Min.	—	6.5	11.0	0.4	—	—	—	0.45
Av..	—	11.2	11.6	0.6	—	—	—	0.77
No. of Anal.	—	36	4	4	—	—	—	35

TABLE III.—(*Continued*)

Tannage		Total ash	Petroleum ether extract	Water soluble	Glucose	Hide substance	Combined tannin	Degree of tannage	Acidity
C....	Max.	0.81	24.8	18.7	—	39.2	28.6	77	0.73
	Min.	0.48	7.0	8.2	—	37.1	12.3	33	0.02
	Av..	0.56	15.6	12.4	0.6	38.0	21.1	54	0.35
No. of Anal.		4	35	4	—	4	4	4	27
D ...	Max.	0.53	21.8	—	—	—	—	—	0.61
	Min.	0.44	6.1	—	—	—	—	—	0.05
	Av..	0.52	12.1	—	—	—	—	—	0.37
No. of Anal.		3	19	—	—	—	—	—	13
E....	Max.	0.70	17.2	—	0.4	—	—	—	1.03
	Min.	0.53	7.4	—	0.4	—	—	—	0.03
	Av..	0.62	12.3	10.2	0.4	—	—	—	0.54
No. of Anal.		3	18	—	3	—	—	—	14
F ...	Max.	—	16.7	10.1	—	—	—	—	1.71
	Min.	—	6.9	8.6	—	—	—	—	0.62
	Av..	0.96	10.7	9.3	—	—	—	—	1.10
No. of Anal.		—	43	2	—	—	—	—	23
G....	Max.	0.21	39.2	—	—	—	—	—	0.45
	Min.	—	5.7	—	—	—	—	—	0.02
	Av..	—	18.8	7.1	0.25	33.7	13.4	40	0.29
No. of Anal.		—	15	—	—	—	—	—	13
H....	Max.	—	19.5	—	—	—	—	—	1.06
	Min.	0.36	7.4	—	—	—	—	—	0.61
	Av..	—	11.2	7.3	—	44.8	27.5	61	0.72
No. of Anal.		—	32	—	—	—	—	—	29
I.....	Max.	—	17.9	—	—	—	—	—	0.61
	Min.	—	6.2	7.3	0.3	—	—	—	0.18
	Av..	—	12.5	—	—	—	—	—	0.38
No. of Anal.		—	30	—	—	—	—	—	25
J.....	Max.	—	32.1	15.3	1.3	—	—	—	1.00
	Min.	0.25	4.5	8.3	0.2	42.2	23.6	56	0.11
	Av..	—	10.9	12.3	0.53	—	—	—	0.47
No. of Anal.		—	38	9	8	—	—	—	36
K....	Max.	—	16.5	14.8	0.56	—	—	—	0.81
	Min.	0.39	5.2	12.9	0.48	—	—	—	0.14
	Av..	—	10.3	13.8	0.52	—	—	—	0.42
No. of Anal.		—	28	2	2	—	—	—	17
L....	Max.	0.53	17.2	—	—	—	—	—	1.06
	Min.	0.29	5.0	—	—	—	—	—	0.30
	Av..	0.41	10.2	—	—	—	—	—	0.70
No. of Anal.		2	26	—	—	—	—	—	23
M....	Max.	—	21.1	10.3	2.5	—	—	—	0.86
	Min.	—	6.1	10.0	0.6	—	—	—	0.02
	Av..	—	11.0	10.1	1.5	—	—	—	0.45
No. of Anal.		—	11	2	2	—	—	—	11

TABLE III.—(*Continued*)

Tannage		Total ash	Petroleum ether extract	Water soluble	Glucose	Hide substance	Combined tannin	Degree of tannage	Acidity
N....	Max.	—	27.0	4.5	—	—	—	—	0.79
	Min.	0.38	23.3	—	—	—	—	—	0.37
	Av..	—	21.8	—	—	—	—	—	0.61
	No. of Anal.	—	4	—	—	—	—	—	4
O.....	Max.	0.42	15.1	—	—	—	—	—	0.70
	Min.	0.32	7.4	—	—	—	—	—	0.06
	Av..	0.37	10.5	13.2	—	38.8	28.5	73	0.42
	No. of Anal.	2	25	—	—	—	—	—	25
P.....	Max.	—	15.8	—	—	—	—	—	0.43
	Min.	—	9.3	—	—	44.7	—	—	0.02
	Av..	—	12.6	—	—	—	—	—	0.25
	No. of Anal.	—	21	—	—	—	—	—	9
Q....	Max.	0.24	17.8	—	—	—	—	—	1.31
	Min.	0.12	6.0	—	0.7	—	—	—	0.62
	Av..	0.20	12.5	—	—	—	—	—	0.92
	No. of Anal.	3	15	—	—	—	—	—	16
R....	Max.	—	9.8	—	—	—	—	—	0.26
	Min.	0.63	5.5	12.9	—	44.0	—	55	0.26
	Av..	—	8.3	—	—	—	—	—	0.19
	No. of Anal.	—	6	—	—	—	—	—	4
S.....	Max.	0.61	15.8	—	—	—	—	—	1.26
	Min.	0.35	5.6	—	—	—	—	—	0.12
	Av..	0.46	10.1	—	—	—	—	—	0.85
	No. of Anal.	4	11	—	—	—	—	—	12
T....	Max.	—	21.1	—	—	—	—	—	1.17
	Min.	—	11.9	—	—	—	—	—	0.22
	Av..	—	14.8	—	—	—	—	—	0.80
	No. of Anal.	—	14	—	—	—	—	—	14
U....	Max.	—	19.4	—	—	—	—	—	0.49
V....	Max.	—	20.1	—	0.44	—	—	—	1.02
	Min.	—	7.7	—	0.36	—	—	—	0.18
	Av..	—	12.6	—	0.40	—	—	—	0.48
	No. of Anal.	—	41	—	2	—	—	—	36
W....	Max.	—	11.3	11.0	—	—	—	—	—
	Min.	—	10.0	10.1	—	—	—	—	—
	Av..	—	10.6	10.6	—	—	—	—	—
	No. of Anal.	—	2	2	—	—	—	—	—
All Tannages	Max.	0.80	39.2	18.7	2.5	44.8	—	77	1.71
	Min.	0.12	2.2	4.5	0.1	33.7	—	33	0.02
	Av..	0.45	12.7	10 3	0.57	40.8	—	56	0.58
	No. of Anal.	24	553	36	33	10	—	8	459

TABLE IV.

Analyses of Retan Upper Leathers.

Received by the Bureau of Standards from November 15, 1917, to November 15, 1918.

Tannage	Total ash	Total grease	Unsaponifiable	Water soluble	Hide substance	Combined tannin	Degree of tannage	Cr_2O_3	Acid	Degree of chrome tannage
A	1.75	25.4	—	2.8	41.0	18.3	45.0	1.44	—	3.51
	2.92	20.2	—	—	—	—	—	1.95	0.53	—
B	2.2	25.8	39.0	—	—	—	—	1 49	—	—
	2.28	30.6	62.0	5.2	31.7	20.5	65.0	1.24	1.10	3.92
	2.70	14.6	—	—	—	—	—	1.46	0.97	—
C	3.62	36.8	—	3.6	33.0	13.6	41.0	2.52	—	7.64
D	3.37	28.1	30.0	3.6	35.6	21.3	60.0	1.49	—	4.18
E	2.44	32.2	45.0	2.9	35.9	16.0	44.0	1.99	—	5.54
	2.44	25.2	—	—	—	—	—	2.03	1.51	—
F	1.80	27.9	—	3.4	31.1	28.2	91.0	1.22	—	3.92
G	2.82	29.5	39.0	2.4	36.3	20.4	56.0	2.47	—	6.80
	2.98	19.9	—	—	—	—	—	1.44	1.62	—
H.....	2.04	26.2	—	5.2	34.0	22.5	66.0	1.01	—	2.97
	2.60	26.0	—	—	—	—	—	1.55	1.51	—
I......	2.12	30.6	20.0	3.3	33.3	20.2	61.0	1.60	—	4.80
	2.12	22.5	—	—	—	—	—	1.32	0.71	—
J......	2.36	31.3	—	1.9	38.8	12.5	32.0	0.99	—	2.55
	1.88	31.5	—	1.2	37.3	17.1	46.0	1.61	—	4.31
K	3.31	16.6	—	—	—	—	—	2.38	1.50	—
L	1.72	29.5	—	—	—	—	—	1.60	0.36	—
M.....	1.87	21.1	—	—	—	—	—	1.46	1.10	—
	1.86	25.9	—	—	—	—	—	1.58	0.80	—
N	3.62	22.4	—	—	—	—	—	2.67	1.22	—
Average of samples analyzed ..	2.47	26.1	39.0	3.3	35.3	19.1	55.0	1.67	1.08	4.56

TABLE V.

ANALYSES OF LATIGO LEATHERS.

Received by the Bureau of Standards from November 15, 1917, to November 15, 1918.

Tannage	Total ash	Total grease	Water soluble	Hide substance	Combined tannin	Degree of tannage	Al_2O_3	Acid
A.....Max.	5.4	17.4	15.1	50.4	17.7	39.0	0.69	0.90
Min.	2.9	14.5	11.9	44.8	12.7	25.0	0.19	0.38
Av..	4.5	16.1	14.0	46.6	15.0	30.0	0.39	0.68
No. of Anal.	6	8	4	3	3	3	3	7
B.....Max.	2.6	19.8	10.6	51.1	29.5	78.0	1.67	0.25
Min.	1.8	11.0	8.1	38.0	8.6	17.0	0.63	0.00
Av..	2.1	15.0	9.3	45.1	18.6	43.0	1.15	0.08
No. of Anal.	5	5	3	3	3	3	3	4
C.....Max.	11.7	18.5	19.2	55.5	8.8	17.0	2.76	1.79
Min.	8.2	11.5	15.8	52.6	2.6	4.0	0.10	0.19
Av..	9.5	15.1	17.3	53.6	4.7	11.0	0.8	1.31
No. of Anal.	13	20	3	3	3	3	8	19
D.....Max.	9.8	21.9	16.7	49.5	2.3	4.0	2.13	—
Min.	8.0	16.7	13.6	46.5	0.0	0.0	1.67	—
Av..	9.1	19.9	14.9	48.0	0.7	1.0	1.80	—
No. of Anal.	3	3	3	3	3	3	3	—
E.....Av..	3.4	11.6	10.8	59.6	4.1	7.0	1.54	1.11
F.....Max.	11.7	19.2	13.6	59.5	6.9	11.0	1.54	1.73
Min.	6.5	8.1	13.3	58.7	3.4	6.0	1.18	1.18
Av..	9.9	13.5	13.5	59.2	5.2	8.0	1.32	1.50
No. of Anal.	5	6	2	3	2	2	3	6
All Tannages Max.	11.7	21.9	19.2	59.6	29.5	78.0	2.76	1.73
Min.	1.8	8.1	8.1	38.0	0.0	0.0	0.10	0.00
Av..	6.4	15.2	13.3	52.0	8.1	17.0	1.16	0.94
No. of Anal.	33	43	16	16	15	15	21	37

TREATMENT OF TANNERY SEWAGE AT THE NATIONAL CALFSKIN COMPANY, PEABODY, MASS.

By R. Harrison Eagles.

The discharge of tannery waste waters into public waterways gives rise to objectionable conditions. Septic action is developed in the stream with the production of a foul stench; the waters become colored inky black with the formation of compounds injurious to fish life; pieces of hide scrap and masses of hair collect along the banks and form breeding places for flies and vermin; in short, the stream which should provide a public playground is transformed into a public nuisance. Prompted by civic pride, and in some cases by the insistence of various health boards and fishery commissions, tanners have long sought for a means of alleviating conditions at a non-prohibitive cost.

In general the waste waters consist of three types of objectionable liquors:

(1) Wastes from the soak vats, which contain organic matter such as hair, dung, bits of fleshings, etc., washed from the green or dried stock, and also bacterial spores which may contain the dread anthrax bacillus.

(2) Beam house wastes, containing colloidal and dissolved hide material, putrescible organic compounds, and large quantities of suspended limes and precipitated organic salts. This type of waste is strongly alkaline, due to unspent lime.

(3) Tanning liquors, containing the spent chrome or vegetable tanning solution, also pickle liquors, wash waters, color wheel wastes, etc., all containing dissolved hide material, leather scrap, sulphuric acid, etc. This type of waste is distinctly acid in character.

Often times these wastes are not even fit for discharge into municipal sewer systems, as these lines are laid with only sufficient grade to carry along a normal load of suspended material, and fail when subjected to the enormous overload contributed by tanneries. The result is a gradual building up of a sediment, necessitating frequent cleaning at high cost.

In the case of the City of Peabody, where the municipal sewers are used to carry away the effluents from the numerous tanneries located there, it had been found that the thorough intermixing

of the various types of wastes in the sewers caused interprecipitation of the dissolved and colloidal organic material; the heavy resultant flocs immediately settling out of the sewage flow and building up in the sewer.

The first logical step in the treatment of the wastes to render them fit for discharge into the sewers, was the installation of sedimentation basins, not only to remove the suspended material, but to allow the various types of wastes to intermingle, causing the heavy precipitation and sedimentation to occur in the basin provided for the purpose, rather than later in the sewers, and producing a combined effluent which was chemically inactive, and would produce no further nuisance.

This was done by the National Calfskin Co. who, some years ago, installed two concrete sedimentation basins, each 56 feet by 28 feet by 7 feet deep. Various baffle arrangements were tried out in the tanks to insure proper mixing and to endeavor to settle out the flocculated precipitate.

The system did not differ greatly from the average sedimentation plant installed at various tanneries, except that special provision was made to insure effectual mixing of liquors of opposite character and ample area for the sedimentation of the resulting precipitate by doubling the capacity specified by the city engineers.

It was found possible to secure the neutralizing effect by regulation of the beam house liquors, that is, by removing the readily settleable "lime grounds" from the beam house vats, and discharging only the supernatant liquor. This had the desired effect of reacting with the acid liquors from the tannery resulting in an effluent which was substantially neutral and chemically inactive.

However, the mechanical difficulties encountered in trying to make the precipitate settle, and in removing the sludge which did accumulate, proved a serious problem, and the cost of cleaning the basins was excessive. Frequent cleaning was necessary because when sludge accumulated in the tank sedimentation ceased and the plant accomplished nothing. The company was obliged to put up with this situation for a number of years as no better method of handling the problem was presented, but finally after considerable experimental work they decided to install a Dorr Thickener, an apparatus which has successfully operated on various other types of industrial wastes, and which has been al-

most universally adopted in the metallurgical industry wherever sedimentation is required.

The Dorr Thickener has for its object continuous sedimentation, with the production of a uniformly clarified overflow, and the removal of sludge at the highest possible density. It consists of a slow moving mechanism set in a circular tank or basin. This mechanism is made up of four radial arms attached to the lower end of a vertical shaft driven by a worm and worm gear. The arms carry plow blades set at an angle which, through the slow rotation of the mechanism, gradually move the settled sludge to the center of the tank, without disturbing sedimentation. The effect of the plowing action is that the sludge is slowly turned over and over as it is moved to the center so that the particles become tightly packed together and the moisture is squeezed out, thus producing a sludge of maximum density.

The bottom of the concrete tank slopes gradually to the center, and the radial arms conform to this slope. Supported on these arms, and surrounding the shaft, is a 6 foot diameter cylindrical sheet iron well extending just above the surface of liquid in the tank. The thickened sludge, as it reaches the center, is forced up into this well by the hydrostatic pressure of the liquor outside the well, and the sludge itself forms an effectual seal so that only thick sludge can find its way into the central well.

The thickened sludge is removed from the well by means of a "stuff pump" delivering to an elevated storage tank, from which it is drawn off into wagons and taken to the dumping grounds. This method of handling sludge is necessary at the National calfskin plant, inasmuch as no space is available for sludge drying beds. It is not possible for any building up of the sludge on the bottom to take place owing to the fact that the bottom of the basin is swept by the thickener arms.

As the sludge is kept constantly in motion septic nuclei have no chance of forming, so the surface of the tank is at all times free from ill-smelling bubbles or floating masses.

The tank is equipped with a peripheral wooden launder into which the clear liquor overflows, spreading out in a thin film, and consequently the velocity of flow through the tank is reduced to

a minimum. One section of the launder, divided off from the overflow portion, is reserved for the sewage feed. The sewage flow enters the tank through this launder, and is uniformly distributed throughout the tank by a baffle. The velocity of flow is cut down as each individual particle seeks its exit at some point in the circular overflow. Reduction of velocity gives the suspended material ample opportunity to settle, there being no supporting currents to carry it along. The peripheral overflow trough collects the effluent liquor and discharges it into a sump which leads to the city sewer.

The thickener unit is preceded by a Dorrco sewage screen for the removal of coarse material such as hair, fleshings, leather scrap, etc., which have a commercial value as fertilizer base This is a self-cleaning revolving drum screen of novel construction. The perforations of the sheet metal shell are 0.1 inch in diameter but, due to the rapid rotation of the drum, particles of even smaller diameter are removed. At the National Calfskin Company the screenings amount to 3,000 pounds per day at 82 per cent. moisture, or 540 pounds of dry solids. The removal of this material makes possible the handling of the sludge through pumps and pipes.

The National Calfskin plant is treating 525,000 gallons of sewage in 10 hours and the following test data have been obtained:

POWER REQUIREMENTS.

(1) Screen and all transmission	3.8 horsepower
(2) Thickener mechanism	0.2 horsepower
(3) Pump	1.1 horsepower
Total	5.1

The plant is removing an average of 75 per cent. of the suspended solids. The sludge amounts to 25,000 pounds daily at 88.2 per cent. moisture or 3,000 pounds of dry solids, making about nine team loads to be hauled to the dumping ground. The effluent produced is clear, golden yellow, and contains but a small amount of red flocculent precipitate. It is practically odorless when fresh, and in every respect suitable for discharge

into the city sewer. The hydrate alkalinity amounts to 0.002 per cent. as Ca $(OH)_2$ and the carbonate alkalinity 0.04 per cent. as $CaCO_3$ thus proving that thorough neutralization has been accomplished.

In addition to the installation just described there is another Dorr thickener plant in Peabody consisting of one Dorrco screen and 3-35 feet diameter thickeners treating the waste waters from the works of the American Glue Company. This plant has been in operation over a year and is producing satisfactory results.

ABSTRACTS.

Wool-Scouring Wastes. *Weekly News Letter,* Aug. 13, 1919. For the Bureau of Chemistry, an appropriation of $9,000 provides for investigations and developments of methods in utilizing wool-scouring wastes that may ultimately mean millions of dollars to the country. This investigation was begun in the fall of 1918 under an allotment from the fund for stimulating agriculture, but the money was not available until late in October, and not a great deal was accomplished. During the war the price of wool grease rose from 2½ cents to 25 or 28 cents a pound, and the price of carbonate of potash rose from 4 or 5 cents to as high as 80 or 85 cents a pound. The result was that a number of plants were installed for the recovery of wool grease and potash salts. Before that time these products had gone to waste and the United States imported all of both products that it consumed. Not only was there a dead loss but the waste material had become a source of serious pollution to rivers and other streams.

The plants built to handle this business during the war, when prices were very high, must install the most economical methods for extracting the by-products of the wool-scouring wastes if they are to continue in operation at the lower prices expected when normal conditions are restored. These economical methods are to be worked out by the Department of Agriculture under the new appropriation of $9,000.

There has been lost every year approximately 50,000,000 pounds of recoverable wool grease. At before-the-war prices this was worth $1,500,000. At present prices it is worth about $8,000,000. There was lost every year, also, about 2,500,000 pounds of potassium carbonate, worth at before-the-war prices $750,000, and at present prices about $6,250,000. Besides these main items, other materials of unknown value are recoverable in wool-scourings, and by far the greater part of this is wasted and seriously pollutes the streams. The work of discovering methods of utilization is well under way and promises to yield methods which will make it possible to utilize the wool-scouring wastes profitably to the country.

Mangrove Bark Resources of the Philippines. *J. R. S. A.* **67**, 566. Mindoro is one of the larger islands of the Philippine group. It is a province by itself and comprises an area of 3,983 square miles. It is distant from Manila a little more than 100 miles, or 12 hours by steamer. Along the shores of this island province are considerably more than 30,000 acres of mangrove swamps, with large trees in practically virgin growth, conservatively estimated to yield 50,000 tons of bark, readily convertible into approximately 17,000 tons of cutch. Why this advantageously situated growth of mangrove should have remained untouched for so long is hard to understand. In a report to the Government on the mangrove bark resources of the Philippines, the United States Commercial Agent in the Islands calls special attention to the Mindoro resources in mangrove, but they are not the only ones in the Archipelago. Altogether there are twenty-one species of mangrove in the swamps of the Philippines—two more than are found in Borneo. These are to be found in the swamps in Bataan or Manila Bay; at the mouth of the Danao River in Occidental Negros; in the municipality of Barotac Nuevo in the Province of Iloilo; and stretches along the island of Palawan, as well as the growths for 45 miles along the shores of Mindanao. The possible cutch production of these swamps is tremendous. Plenty of cheap labor is available, and there is no duty to be paid on the extract entering the United States. The tannin content of the barks is stated to run from 12 to 35 per cent., and to be on average quite as satisfactory as that of the Borneo mangroves.

At the chemical laboratory in the Bureau of Science, Manila, a cutch was made by leaching from the finely-ground bark in cold water, the solution being reduced to dryness in a vacuum. The resulting cutch was dry, solid, brown in color, and the fracture was brilliant—almost metallic. It was easily and completely soluble in water.

Analysis of barks from Mindoro show tannin content ranging from 9.6 to 28.2 per cent. Those from Mindanao show content from 8.8 to 27.2 per cent. The highest amount of tannin found in samples of Borneo bark was 32 per cent.

While many of these swamps are large enough to be commercially attractive, those of Mindoro seem at present to offer the best inducements. They are directly controlled by the Bureau of Forestry and may be worked under license. The timber growths of the Philippines are carefully conserved, so that they could not be worked for bark alone, but the demand for piles, poles and fire-wood is so great that the stripped timber could be readily and profitably marketed. Another basis upon which to work would be to buy bark from independent firewood cutters, who would welcome such a market. Still another possible method would be in conjunction with one of the large lumber concerns. One of these is operating in Mindanao, and, at the date of the report, was not using the bark at all.

Production of Divi-Divi in Dominican Republic. *J. R. S. A.*, **67**, 567. Divi-divi is the commercial name for the astringent pods of a leguminous shrub indigenous to the Dominican Republic. The plant is between 20 and 30 feet in height and bears white flowers. The fruit of this shrub

is a bean, averaging 2 inches in length, 1 inch in width, and about 1/8 of an inch in thickness. It contains about 30 per cent. of a tannic acid, used in the manufacture of leather. The bean ripens and falls to the ground from November to April. If it rains while the beans are on the ground they are ruined. Large quantities are lost in this manner, as November and December are rainy months in the Republic of Dominica.

Whole families of the poorer people devote their entire time to gathering divi-divi beans and bringing them to market. It is difficult to state the average yield per shrub; some produce as many as 70 pounds or more, and others of the same age yield only half that quantity.

Almost all of the divi-divi shrubs in the Puerto Plata district are to be found in the arid lands of the Province of Monte Cristi. They are not cultivated, but grow wild over vast sections of the province. The town of Monte Cristi, on the north coast near the Haitian border, is the center of the industry, and is the port from which most of the product is exported. Divi-divi is usually packed for export in jute sacks, weighing from 110 to 125 pounds gross. It was formerly shipped to some extent in bulk in sailing vessels, but this mode of shipment has been discontinued as it was not found practicable.

The value of this product is determined by its quality and appearance; large, plump and ruddy beans are in good demand, while small, black and broken beans are unsaleable. The annual exports of divi-divi from Monte Cristi formerly exceeded 2,000,000 pounds, but of late years they have fallen below these figures. The decline in the output is attributed to a species of orchid, which lives on the shrubs. This parasite reduces the production and often kills the plant. Nothing has been done to eliminate this pest, although it has spread at an alarming rate, so that there is hardly a shrub which is not infested with it.

Prior to the war divi-divi was exported to Hamburg almost exclusively; in the past few years, however, it has found a ready market in New York. The prices were formerly fixed in Hamburg at from 9 to 12 marks per 50 kilos (roughly $40 to $55 per ton), but last year the price was from $50 to $55 per ton (2,000 pounds) f o. b. New York.

The Relative Value of Tanning Materials. By H. G. BENNETT. *Leather World,* July 17, 1919. The value of tanning materials is a subject which appeals to all of us, and one of extreme importance to the trade, and perhaps there is room for some difference of opinion. Now, our knowledge on this question has hitherto been mostly gained by bitter experience in practice, and, as you know, that is a very slow method because it was months before one could see and ascertain the results of the experiments, and it is often a very costly method, because if the experiments are adverse and the leather made is unfavorable there was very much leather affected, and in addition it is often a very inconclusive method. Very often one's practical experiments in the yard makes it uncertain which factor should get the credit or discredit, and it is not

going too far to say that the relative value of tanning materials has been determined in the past largely by prejudice.

We are all aware that the two extracts, quebracho and chestnut, each containing 30 per cent. tannin, are not of equal leather-forming value. What is the difference between them? How can we compare and contrast them? Further, how can we determine their practical value?

Some years ago some useful work on this question was done by one or two chemists. Dr. Parker compared the weight-giving properties of myrobalans, Greek and Smyrna valonia, etc., and Youll and Griffith compared different materials also. These operators did their work before the vast development of colloidal chemistry in recent years. The principle of their method was to compare the weight obtained in small scale experiments in a sort of miniature tan-yard. If results in the yard are likely to be inconclusive so much more, therefore, are the results of a miniature tan-yard liable to be misleading. Since these papers appeared practically no work has been done on the subject.

In the last decade or so, the main principles of leather formation have been made much clearer by the enormous development in our knowledge of colloids—which include substances like hide and tan. Von Schroeder, in 1908, first pointed out that the hide gel in a tan liquor obeyed the ordinary adsorption law. He experimented with powdered hide in gallotannic acid, and while he showed on the whole the adsorption law was obeyed, there were certain conditions under which there was divergence from the law, *e. g.,* lapse of time brought about secondary changes, and there was also divergence in stronger liquors owing to the viscosity of the liquor becoming an important factor. Other advances in knowledge not only confirmed this, but also put the matter in a much clearer light, and early in 1917 in a paper published on a cognate subject I suggested that the weight-giving properties of any particular tanning material would be better expressed by its adsorption isotherm than in any other way. Since then I have been able to confirm this opinion by experimental work.

The adsorption law is expressed by the equation:—$y = mac^{1/n}$

Where y = amount of tan taken up
m = weight of hide
a = constant for conditions of experiment
$C^{1/n}$ = mathematical function of strength of liquor the hide comes out of.

Taking such a quantity of hide that $ma = 1$ the $y = c^{1/n}$; or the amount of tan taken up by that amount of hide is equal to the mathematical function of the strength of the liquor from which it is removed.

Simplify still further by taking n to equal 2, which is approximately true for quebracho extract and gallic acid. Then $y = \sqrt{c}$, or y equals the square root of the concentration of the liquor the hide is removed from.

Now, if $y = 1, 2, 3, 4,$ etc.;
then $c = 1, 4, 9, 16,$ etc.;
and $(y + c) = 2, 6, 12, 20,$ etc.; being equal to the original concentration of the liquor.

This illustrates the operation of the adsorption law. It will be seen that if the amount of tan to be taken up is to be twice as great, then the liquor that the hide is to be put in must be three times as strong. If the amount of tan to be taken up is to be three times as great then the concentration of the liquor the hide is put in is to be six times as strong. This illustrates that the amount of tanning matters that are absorbed increases very much more slowly than the strength of the liquor it is necessary to put the hides in. It follows, therefore, that as the strength of a liquor gets past a certain practical limit, there must be big increases in its strength in order to get a small increase in weight.

My experiments have been to compare the resultant of different materials in order to compare their weight-giving properties, the adsorption curve for each common tanning material under ordinary tanning conditions.

Various infusions of different strengths of the material to be tested were taken. It was found convenient to have one double the strength of the other. Into these solutions of known strength, add 1 gram of hide powder, prepared as for analysis. Agitate at least 30 minutes; to get equilibrium, filter off hide powder and determine solids unadsorbed. It is rather like ordinary analysis, but with only 1 gram hide powder. The conditions are very analogous to conditions in the yard, a small amount of hide and an excess of tan.

The object of the experiments was to determine a and n, which are characteristic of the different tanning materials, under the conditions of experiment, and to determine the nature of the adsorption isotherm under exactly comparable conditions.

The results are only safe if a good number of experiments are made. These experiments were done in triplicate, three experiments side by side, repeated several days running in order to be sure of getting a safe average.

For example, the experiments with chestnut extract were conducted in triplicate on each of the days, and resulted as follows:

			a	n
Dec. 31	...	...	0.742	1.26
Jan. 6	...	...	0.739	1.26
" 21	...	...	0.842	1.13
" 24	...	...	0.812	1.20
" 25	...	...	0.812	1.22
" 28	...	...	0.770	1.24
			0.79	1.22

Therefore, the weight-giving properties of this particular chestnut extract are given in the expression:

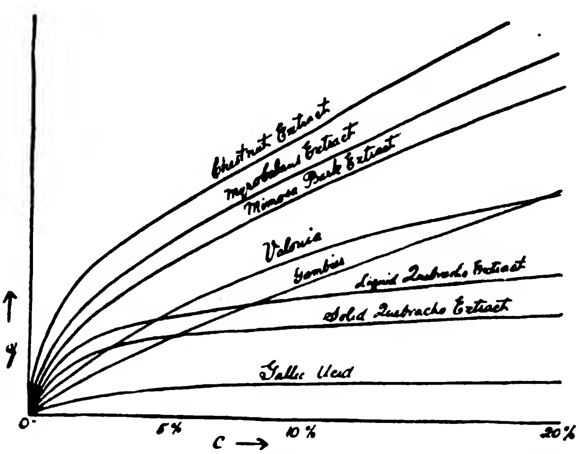
$$\frac{y}{m} = 0.79\ C^{\frac{1}{1.22}}.$$

The agreement was better than expected, because the conditions were occasionally bad, the hide powder was too powdery or too lumpy, etc. Similar protracted experiments with other substances gave the following comparative table of typical known tanning substances:

	a.	*n*.
A chestnut ext.	0.79	1.22
A mimosa bark ext.	0.75	1.45
A myrobalans ext.	0.75	1.30
A mixed ext.	0.64	1.59
A liquid quebracho ext.	0.62	1.90
A sample of valonia	0.60	1.61
A solid quebracho ext.	0.45	1.82
A sample of gambier	0.36	1.15
Pure gallic acid	0.15	2.04

The figures for *a* show the weights that will be obtained in weak liquors, say a fresh liquor of 4° B., *n* determines the increase of weight obtained by increasing the concentration of the liquors. If *n* is small a better weight will be obtained by further concentration; if *n* is large, increase of strength in liquors won't give much extra weight.

Taking *a* and *n* together the following comparative adsorption curves are obtained for the various tanning materials experimented with:



Comparative weight-giving curves for the particular samples tested.

It will be seen that chestnut extract, myrobalans and mimosa bark, are the best weight-giving materials, whether you take them in weak liquors or strong liquors. Another deduction is that valonia is a second-rate material from the standpoint of weight.[1] It is not quite so good even as quebracho in weak liquors, and about the same as gambier in strong liquors. Another deduction is that it is evident there is not much point

in using quebracho in strong liquors, and I may say there is not very much point in using some quebracho extracts at all.

In gambier, the curve is rather a surprise. It is not a weight-giving material at any stage, but curiously enough it shows best results in the strong liquors one cannot afford to make. It gives a very bad weight indeed in weak liquors, and I should not think that gambier is often used as a weight-giving material, especially in these days.

Another deduction we can draw is that if gallic acid is at all typical of astringent non-tanning materials, non-tans give a little weight, but give very little in either weak or strong liquors.

The determination of the adsorption curves for a tanning material is a very useful procedure, a method of testing tanning materials, not for checking the strength of supplies bought on contract, but from the standpoint of finding out their practical value for use in weight-giving; a method of comparing two extracts, two different quebracho extracts, two chestnut extracts of two mixed extracts, and a method of classifying tanning materials according to their weight-giving powers. Further, it is a means of finding out how to use a tanning material; whether you ought to put it in layers, handlers or suspenders, or whether it is worth using at all.

I am quite aware that some eminent leather chemists have poured scorn on the adsorption theory. In my judgment and experience it gives the best explanation of the phenomena of tanning, supplies sound guiding principles for practical application, a ready explanation of apparent anomalies which constantly appear in practice, and a fertile field for investigation and research. I venture to say without the slightest hesitation, that the leather chemist who thoroughly understands the applications of the adsorption law should be in a position to make any kind of leather he wants, and to make it well. The man who understands and can apply these two generalizations of colloidal chemistry will be the practical tanner of the next generation.

1. [The author disregards the time factor in making his deductions as to the weight-giving properties. With valonia, for instance, it is claimed that its value as a weight-giving material is due to changes brought about by fermentation. Editor.]

Iron Tannage. (Part 1.) JOSEF JETTMAR, *Le Cuir* 8, 74 (1919). A review of patent specifications of iron tannages from that of Ashton in 1794 to the present. This has already been treated by Casaburi (cf. This JOURNAL 14, 423 (1919)). Much energy has been expended in attempts to devise an economical process for the oxidation of ferrous sulfate to the ferric state for use in tanning. Difficulty was experienced in getting the iron fixed so that it would not wash out when the leather became wet. If too much acid is left in the leather, it becomes brittle upon drying, but one cannot neutralize as in the case of chrome leather with alkaline salts because the iron will wash out. This trouble was overcome by the use of neutral salts. (The reason for this is probably to be found in the method for preparing colloidal ferric oxide. If alkali be added very slowly to a solution of a ferric salt, it is often found that no precipitation

of iron takes place, but the solution assumes a very deep red color through the formation of colloidal hydrated ferric oxide. When this state is reached, the addition of common salt or even of a small amount of HCl will cause precipitation of the iron. Evidently the iron in an iron-tanned leather readily assumes the colloid state, but colloidal iron is positively charged and so is the slightly acid hide; the two would, therefore, repel each other and we should expect the iron to wash out readily. The addition of neutral salt causes precipitation of the iron, which then will remain in the leather during the washing to remove free acid.—Abstractor.)

(Part 2, *concluded.*) *Le Cuir*, **8**, 106 (1919). It is stated that if a skin be tanned in basic ferric chloride and dried without further treatment, it will shrink to such a condition as to be worthless for practical purposes. But, if such leather be subsequently treated with formaldehyde, a very serviceable leather results. Sheepskins thus tanned will replace chamois. With this treatment, an iron chloride liquor gives a leather containing no mineral acid, but, on the other hand, an iron sulfate liquor does not give a neutral leather. Comments are made upon the recent patents of Röhm and of Kanet. The last patent dealing with iron tannage to be taken out in Central Europe was one by Mensing (Swiss, 75775—1918), who attributes difficulties obtained by other methods to the presence in the iron liquors of ferrous salts. In his method he prepares a liquor free from ferrous salts by using and maintaining an excess of the oxidizing agent in the liquor during the tannage. Jettmar will be interested to learn of the progress made in Allied countries.

J. A. W.

The Leather Industry in Indo-China and Southwest China. GASTON LHOMER. *Le Cuir*, **8**, 119 (1919). Progress has been very slow because the demand for leather from the natives is small. They go barefoot and, therefore, need no shoes and the factories use very little belting. The need for tanneries came with the influx of Europeans. The first really modern tannery was started by a French company in 1912 at Hanoi. This firm was able to supply most of the country's needs during the war, when the only imports were sole leather from Java, box calf from America, and some equipment from Japan. The hides available are rough, badly branded, and come without horns, ears, snouts, hoofs, or tails, and are nearly completely fleshed. They weigh about 17 kilos each when fresh; as a rule they are much scratched, scabby, and pricked. The chief tanning material is mangrove bark, which gives a red colored leather which will not bleach. For the better grades of leather, on account of color, native varieties of chestnut and oak barks are used. The finished leather is usually strong in the butt, although very empty in the flanks. Transport facilities are so poor that it is difficult to exploit the resources of the country in tanning materials. *Lim* wood with 5 per cent. tannin and the root of the *cu-nau* with 9 per cent. tannin are also available. In southwest China the chief tanning materials are nut-galls and *cu-nau*.

J. A. W.

The Stability of Tanning Materials. A Tanner. *La Hallé aux Cuirs*, Aug. 10, 1919. Tannin content alone is an unreliable index of the value of a tanning material; such factors as leather yield, rate of penetration, price, and stability must be considered. The argument is supplemented by a review of Paessler's paper on the *Essential Qualities of Vegetable Tanning Materials* (This JOURNAL, 6, 316 (1911)). J. A. W.

PATENTS.

Apparatus for Stretching and Drying Leather. U. S. Patent 1,310,148. MAX STEINHARTER, Philadelphia. A stretching apparatus, which comprises a netting the surface of which is dished, a frame provided with curved braces for holding and supporting said netting, and a plurality of clamping devices.

Waterproof Substitute for Leather and the Like. U. S. Patent 1,310,624. HERBERT F. KENWORTHY, Stoughton, Mass. A fibrous and filmy fabric having pores filled with a viscous lubricant having mixed with it a small proportion of hard drying wax, sufficient in quantity to produce an elastic film by oxidation when exposed at the surface.

Waterproof Glue. U. S. Patent 1,310,706. ALFRED C. LINDAUER, Madison, Wis. A waterproof glue comprising casein, lime, sodium hydroxide, less than 1 per cent. of a non-oxidizing hydrocarbon oil, and water.

Tanning Apparatus. U. S. Patent 1,310,749. CHARLES JOHN GLASEL, New York, N. Y. In a tanning apparatus, the combination with a rectangular tank of water-tight construction, of trunnions forming a horizontal axis for the tank, bearings for the trunnions, sectional hanging bars for the hides, pins in the bars, means for rotating the tank, and means for filling the tank when closed with liquid for tanning and circulating the same through one of the bearings and its trunnion.

Artificial Leather and Method of Producing It. U. S. Patent 1,308,231. RICHARD F. DYER, Providence, R. I. Filed Aug. 14, 1918. Serial No. 249,908. 10 Claims. (Cl. 91—70.)

Process of Preparing Patent Leather. U. S. Patent 1,309,863. JAMES MCDONALD, Cincinnati, Ohio. Filed Apr. 18, 1917. Serial No. 162,862. 5 Claims. (Cl. 91—68.) That process of treating leather which consists in treating a hide with desired fluid, wiping off the hide, and then applying a brush, of a length to bridge the hide, with a circular movement of the entire brush in a plane parallel to the surface treated, whereby among other things, the brushing of the hide is so done as to apply equal brushing pressure at a like speed to all points of the hide.

Tanning. British Patent 124,718. RAMPICHINI F. & C., 15, Rue St. Ambrogie, Milan, Italy. Feb. 24, 1919, No. 4571. Baths containing enzymes of animal or vegetable origin, intended to emulsify fats and peptonize albuminoids in hides immersed therein, are provided with antiseptics which prevent any foreign fermentative or bacteriological action taking place. The antiseptics may be inorganic or organic compounds, *e. g.* arsenious anhydride, salicylic acid, phenol, benzo-naphthol, etc. Tanning material or other substances having a merely chemical action may be added to the bath.

Removing Bark from Logs. British Patent 124,854. HELLSTROM, G., Imperial Buildings, 56, Kingsway, London. Jan. 29, 1918, No. 1689.

Tanning. British Patent 126,853. JOHNSON, R., The Beeches, Frodsham, Warrington, GREGORY, W., 102, Churchfield Terrace, Runcorn, and MORRISON, J. A. S., The Limes, Frodsham, Warrington, July 2, 1918. Apparatus for slaking and mixing lime and transferring it to pits.

Leather. British Patent 126,938. DORAN, E. T., Arendal, Norway. Oct. 4, 1918, No. 16175. Hides are hardened, etc., by treatment with lead acetate. The hides after treatment, as in a chrome bath, are dried and placed in a bath containing a solution of lead acetate preferably at a temperature of 18-20° C. Acetic acid and barium acetate may be added. Before immersing in the acetate bath, the hides may be subjected to swelling in acids.

Stretching and Drying Hides. British Patent 127,386. POLINKOWSKY, L., 70, Westbourne Terrace, Hyde Park, London. May 25, 1918, No. 8670.

Journal of the

American Leather Chemists Association

Vol. XIV NOVEMBER, 1919 No. 11

W. K. ALSOP . . . . Editor and Manager
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Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $6.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized July 16, 1918.

LEATHER CHEMISTRY IN JAPAN.

By Lloyd Balderston.

Received May 24, 1919.

Hokkaido Imperial University dates from April, 1918. Previous to that time the institution at Sapporo had been a College of Agriculture, other departments of the Tohoku Imperial University being at Sendai, some hundreds of miles further south. With the establishment of a medical school at Sapporo came the incorporation of a new university with the above title.

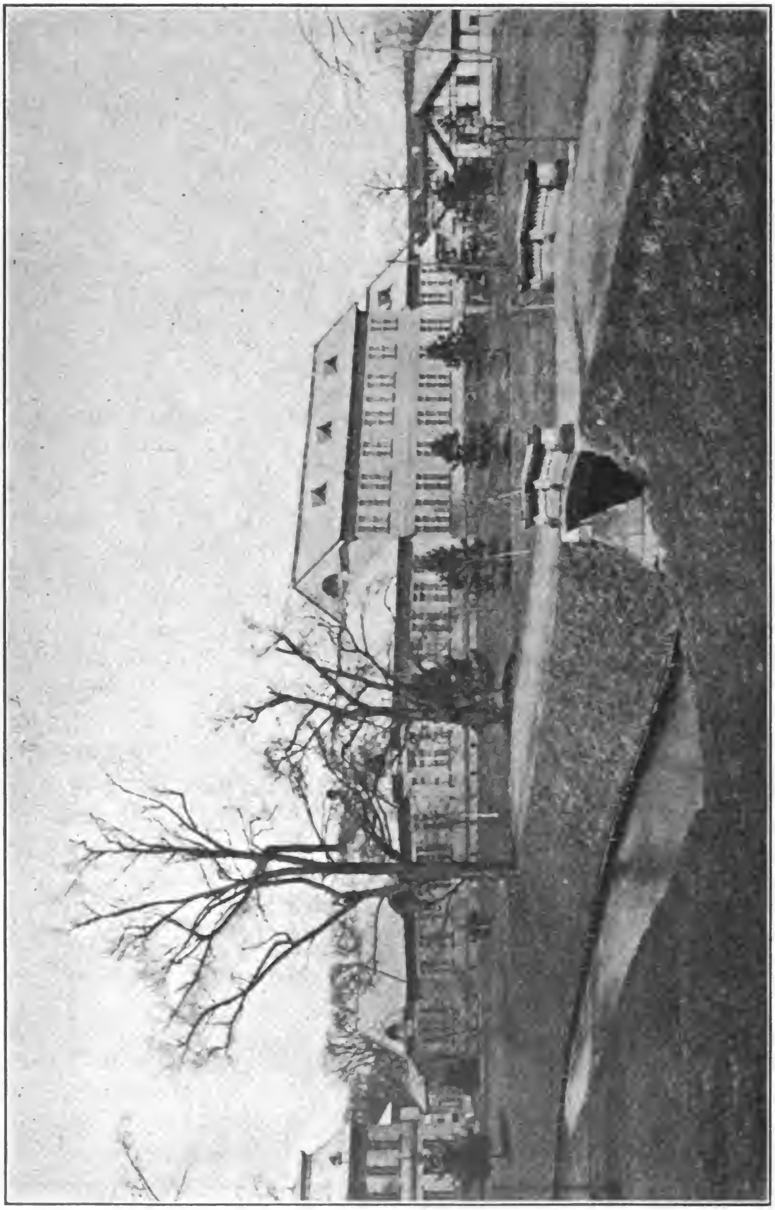


Fig. 1.—Zootechny Building.

The College of Agriculture embraced five subsidiary schools beside the departments of university grade. Roughly, these subsidiary schools correspond to the first two years of a first class American college course. They are, (1), the preparatory course for the University, (2), the school of practical agriculture, (3), the school of practical forestry, (4), the school of civil engineering, and (5), the school of fisheries.

Entrance to the university proper is only through the preparatory course above named. In the College of Agriculture are four main departments, Agriculture proper, Agricultural chemistry, Forestry and Zootechny. The department of zootechny is divided into two sections, veterinary medicine and animal industries. As a part of the latter section, a department of leather chemistry and technology was planned some years ago, and a substantial building erected for an experimental tannery. The illustration Fig. 1, shows the zootechny building, with the tannery at the extreme right. The corner showing at the left is a part of the forestry building. The second floor of the zootechny building has two museums, a library and dark-room. The ground floor is occupied by lecture rooms, laboratories and offices.

When I arrived in November, 1917, the tannery was equipped with a large wash-wheel, a pin drum, a glazing jack and a buffing machine. These pieces were built and installed by an Osaka firm. We have since added a paddle and six small concrete vats. The vats are 3 feet long, 4 feet deep and 6 inches wide, each one holding two sides hung over sticks. The interior of the tannery is shown in Fig. 2.

No course of lectures on leather subjects had been given at the university, and no special apparatus for the analysis of leather and tanning materials was in hand. The problem presented to the newcomer, therefore, was to design apparatus for the laboratory, and to put before the students as much as possible of leather chemistry and leather making in three lectures a week for one term and two for two terms. One of the requirements for graduation is a thesis, which must represent a lot of work. Two students wished to do theses in leather subjects, and to start work at once. As we had no facilities for dealing with tannin or vegetable-tanned leather, I was obliged to set both at work on chrome leather topics.

Fig. 2.—Interior of Tannery.

Some of the difficulties encountered in securing the necessary apparatus were alluded to in a previous paper.[1] The evaporator and dryer and the extractors were finally installed, and then it turned out that they could only be used in the day time, because the water supply is operated by compressed air, and the pressure is not kept up at night. It was a matter of months to provide a subsidiary tank on the second floor, with a ball valve, to furnish water for the condensers of the extractors and for the oven. By the time this was completed, the grinding apparatus was ready, and everything seemed in shape for beginning tannin analysis. But here came another surprise. The insurance department stepped in with an absolute veto on leaving gas burners running all night, in spite of the complete precautions which had been taken to avoid risk from fire. Finally a sheet-iron hood, three sides and roof, with tile floor, was prescribed. When this was completed, late in January, we were at last really ready to do some work on tannin.

The extractors are of the Reed type, with a capacity of 2½ liters, so that they may be used for extracting sumac and such materials to 2 liters without refilling. They work perfectly also for barks, where ½ liter is collected outside and another ½ run with the reflux condenser over night. The loss is very small, and if 1,100 cc. of water are put in at the start, both the loss and the water retained by the bark are provided for. When the extraction is finished, the water from the bark container is drawn off by opening the outside cock. A few cubic centimeters are used to test for tannin. The rest is set aside with which to rinse out the extractor after pouring its liquor into the receiving flask.

The evaporator and dryer, or oven, is of the type described in the JOURNAL for October, 1914, (Vol. 9, p. 442). The gable ends are double-walled, also both slopes of the roof. The vertical front and back walls are not hollow. Steam enters the lid through the hollow hinge at the left hand side, shown in Fig. 3, and leaves at the other end into the condenser shown at C in Fig. 5. The opening through the hinge should have an area of at least 1 square inch for an oven 16 by 24 inches in size. This one was made up at first with a hole about one fortieth of that size, because of the superior wisdom of the maker. After one rebuilding

[1] JOURNAL, July, 1918.

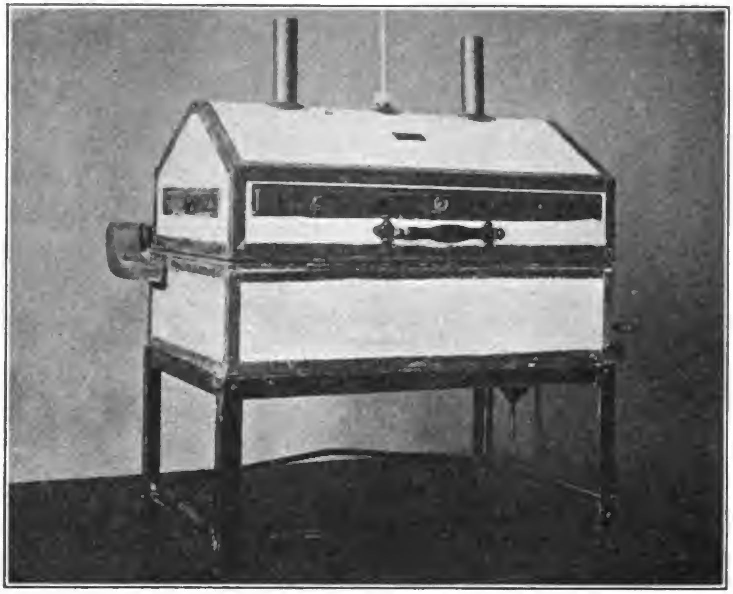


Fig. 3.—Evaporator and Dryer, showing hollow hinge

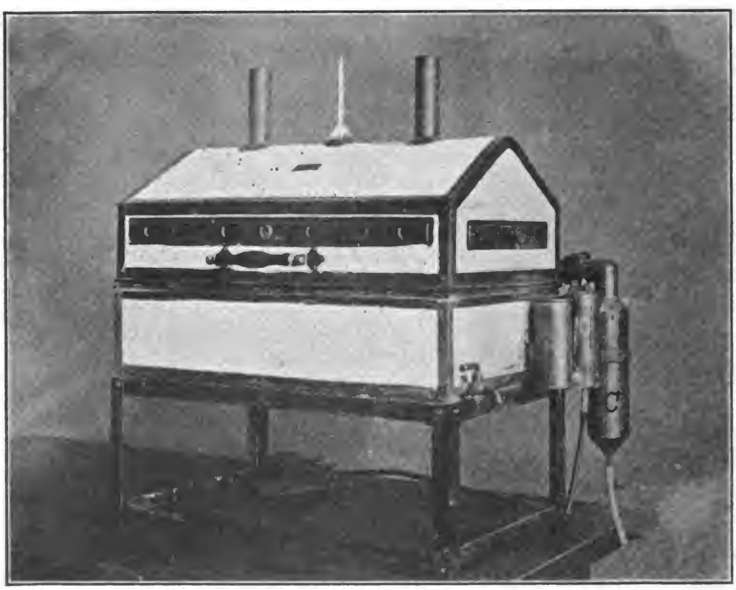


Fig. 4.—Evaporator and Dryer, showing condenser and constant level.

the size of the hole had risen to about ⅓ of a square inch. This proved insufficient, as pressure was caused in the water container, forcing out the water. Rebuilt again, the hole now has a cross-section area of about a half of 1 square inch. Once in a while the water would blow out for a few minutes, and then a flood of cool water comes in, running the temperature of the oven down to 70° C.

As it seemed impossible to get the hole made large enough without making an entire new oven, we tried putting a check valve on the constant level arrangement. This works perfectly, and now the temperature of the oven can be kept at 95° C. or above indefinitely. Fig. 5 shows the plan. When the pressure

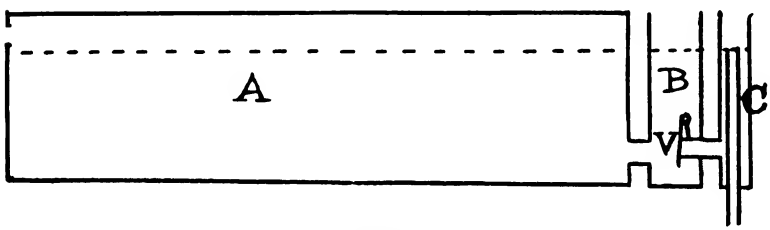


Fig. 5.

rises in A, the valve V closes, and the water rises a little in B. Presently the pressure subsides, the water in B falls, and more water flows in, from C. The supply of water to C is from the condenser, and is preferably hot. There is no necessity for the intermediate vessel B, as the valve might as well be inside of A or in the pipe between A and C. This method was adopted because, B being already fastened in place, it seemed easiest to arrange it so.

I presume that all leather chemists have been troubled by the corrosion of soldered seams under the continued action of steam. The lid portion of a combined evaporator and drier always needs mending once a year or oftener, in my experience. Joints made with "hard solder" do not corrode, but coppersmiths say it is not practicable to braze seams on copper of the thickness used for apparatus of this kind. It has been found, however, that when the soldering is done with pure tin instead of the ordinary half

tin and half lead, the rate of corrosion is much reduced. The additional cost in labor and material of doing the soldering with tin will be much more than repaid in satisfaction and in less frequent repair bills.

The order for this oven called for asbestos lining for the front and back walls. The maker put it all over the lid on his own motion, and we afterward covered the base to save heat. The holes to admit air were prescribed of fixed size, but that did not satisfy the maker, so without consulting anyone he put on the fancy slide affairs shown, which are not an advantage for tannin analysis. If the oven is used for some other purpose, where there is almost no water vapor to dispose of, and where a somewhat higher temperature is desired, the slides may be closed and the chimneys plugged.

The extractors for determining water soluble in leather are of the type described in the JOURNAL for April, 1918.

The arrangement of circular saws for grinding leather is similar to the apparatus in use in various American laboratories. There are four saws, side by side, with teeth 3/8 of an inch apart. The motor is of 1/2 horsepower. This motor also drives a mill for grinding bark, etc. Coffee is not used to any extent in Japan, so that the power coffee mills such as American laboratories use for bark grinders are not to be had. After long waiting we secured a mill made here in imitation of a Krupp mill. It does well, but will not take material in pieces more than 1/4 of an inch in size. We use the saw for any bark samples which are in large enough pieces to be handled in that way.

I am aware that the saw method of grinding leather is not approved by all leather chemists, because of differences of results between samples so prepared and those which are sliced. No rapid method of slicing which can be applied to any and every sample of leather has been devised, so far as I know, and pending an official decision on method of division of leather for analysis, I decided to install this apparatus, which will still be very useful even if we have to discontinue its use for leather.

Two members of last year's graduating class returned this year for one term of special work, and are now employed as chemists by leather firms. Two men of the Class of 1919 are

already engaged for positions in which the little they have learned of leather matters will be of service, so the leather department is already beginning to justify its existence.

HOKKAIDO IMPERIAL UNIVERSITY,
Sapporo, Japan, April, 1919

THE DEVELOPMENT OF THE CHROME TANNING INDUSTRY IN THE UNITED STATES OF AMERICA.*

By Douglas McCandlish.

As the United States has been so closely associated with the chrome tanning industry since its inception, it seems appropriate, in considering the subject as a whole, that special consideration be given to the part taken by that country in originating and developing what is a comparatively new method of tanning. It is not surprising to find that the chrome process was favorably received in the states, for its outstanding feature, that of producing a serviceable leather in considerably less time than it could be produced by prevailing methods of tanning, appealed strongly to the Americans' inborn desire for speed. The time necessary for tanning by either the vegetable or chrome process is governed by several factors, such as the thickness of the skins, the kind and condition of the tanning liquor, etc., but it may be said that while the older system of vat tannage with vegetable materials required weeks or months, chrome tannage may be completed in as many hours as the former process required days.

The commercial employment of chromium compounds as tanning materials in America commenced about 1884, when Augustus Schultz of New York, was granted a United States patent for what he described as "An improved process for the tawing of hides and skins." Schultz was born in Germany in 1834, and moved to America in early youth. He was not a tanner, but while employed as chemist to a New York dyestuff agency was asked by a friend if it were possible to produce a leather that would not cause corset steels to rust, as ordinary alum tawed leathers did. His investigations resulted in the production of a leather of the desired quality, and the method suggested is now

* Reprinted from *J. S. C. I.*, **38**, 265T (1919).

universally known as the "two-bath process." In this method of tanning, the skin is impregnated with chromic acid, which is readily absorbed by the skin fibers in the first bath. The chromic acid is subsequently reduced in a second bath to a basic chromium salt, which is the actual tanning agent. A mixture of sodium or potassium bichromate with hydrochloric or sulphuric acid is used for the first bath, and a mixture of sodium thiosulphate with either of these acids constitutes the second or reducing bath.

The practical application of the process presented many difficulties, and while these were gradually overcome fairly large fortunes are known to have been lost by the American pioneers in the chrome tanning industry. Many attempts were made to circumvent the patent specifications, and various substitutes were suggested to replace the thiosulphate and acid bath. However, none were as satisfactory as the latter, and they did not find extended application.

Several years before Schultz patented his method, Professor Knapp in Germany had described a process for making chrome leather by the use of basic chromium chloride solution, made by dissolving precipitated chromic hydroxide in hydrochloric acid and rendering the solution basic with sodium carbonate. He wrongly stated that the leather so produced was no more resistant to water than ordinary alum-tanned leather, a mistake difficult to understand, as Knapp was ordinarily a painstaking worker. As a matter of fact, while alum-tanned leather will dry hard and horny after treatment with cold water, on account of the unstable nature of alum tannage, chrome leather tanned by the method suggested by Knapp withstands the action of boiling water without any apparent sign of injury. Martin Dennis, of Newark, N. J., evidently became aware of the possibilities of this method and in 1893, was granted a patent for a basic chrome tanning liquor which closely resembled Knapp's basic solution. By means of such a liquor, properly prepared hides and skins may be converted into very satisfactory leather, and as the tannage is completed in one solution, this system is known as the "one-bath," as distinct from Schultz's "two-bath" process. Although the ultimate tanning agent in both processes is the same, *i. e.*, a basic chromium salt, there is one essential difference between the methods. In the two-bath process finely-divided sulphur, liberated

from the thiosulphate-acid solution in the second bath, is deposited in and upon the fibers of the leather, giving a certain characteristic softness not readily obtained by the one-bath tannage.

The processes described form the foundation upon which the chrome tanning industry of the United States has been built While the advantages and disadvantages of chrome and vegetable tanned leathers have been the subject of many controversies, the fact remains that so far as upper leather is concerned, the former has largely supplanted the latter during the past 20 years in the United States as well as in this country.

Before considering the development of the industry, a brief outline of the operations preceding and following the actual tanning of light leather is necessary.

The raw skins are first washed with water or soaked in dilute sodium sulphide solution, the treatment varying with the method of preservation of the skins. They are then subjected to the action of a weak alkaline solution which loosens the hair roots sufficiently to allow the hair to be rubbed off the skin with a suitable dull-edged unhairing tool. As milk of lime has been universally used for this operation, it is commonly known as the "liming" process. The lime left in the skin is removed by washing with water, dilute acids being sometimes used to facilitate its removal, and the stock is then puered or bated in a fermenting infusion of dog or pigeon manure. The skins are now ready for tanning. When this is completed, the leather is neutralized with a weak alkali, washed, dyed, and fat-liquored, the latter operation supplying the necessary lubricant to the fibers in the form of an oil emulsion. The leather is dried, softened by mechanical means, and finished by one of a great variety of methods according to the particular purpose for which the leather is intended.

It is by the gradual improvement of the various processes described, rather than by any revolutionary changes, that progress has been made in the chrome leather industry in the United States, and an attempt will be made to describe a few of the more important advances in American practice.

Considerable changes have taken place in the methods of depilating. The use of sodium sulphide, either alone or in con-

junction with lime, has entirely supplanted the use of milk of lime as the medium for loosening the hair. Not only is the time required for the operation shortened considerably, but, what is more important, the hide substance is conserved and a better grade of chrome leather results. Some tanners find it profitable, for certain classes of leather, to use sodium sulphide of such concentration that it dissolves the hair from the hide. The destruction of the hair, itself a valuable by-product, may appear at first sight to be uneconomical, but a process has been patented and is in operation in connection with at least one tannery, for the recovery of the dissolved nitrogenous matter for fertilizing purposes. The sulphide solution containing an accumulation of dissolved hair from several lots of hides is acidified, and the liberated insoluble amino compounds are found to contain a sufficient proportion of nitrogen to make the process profitable, at least when war-time prices for fertilizer prevailed. It seems reasonable to expect that nitre-cake might be satisfactorily substituted for sulphuric acid, and the process made more profitable.

The old system of puering or bating with animal excrements has been almost entirely superseded by methods having none of the objectionable features of the old methods. The most successful artificial bates are those prepared on lines suggested by the researches of J. T. Wood, the active principle of these being trypsin, obtained from the pancreas of cattle. Although numerous previous attempts had been made to prepare substitutes which would satisfactorily replace dog manure for puering goatskins, the most difficult class of skins to puer, none but the class described have produced the desired results.

The actual tanning processes have been greatly improved. In the one-bath system, a better understanding of the necessary relationship between the basicity of the liquor and the condition of the raw pelt has helped to do away with a great deal of the uncertainty which existed in the earlier days. In this connection American chemists are doing good work in elucidating the problems of chrome tanning. As an indication of the interest in the scientific side of the industry, a well-known firm of tanners recently showed a commendable spirit by placing a considerable sum of money at the disposal of an American University for the purpose of investigating certain fundamental principles of the chrome

tanning process, and the results of the research are to be published for the benefit of the trade as a whole.

The fat-liquoring of leather was formerly carried out with emulsions of animal and vegetable oils in soap solution. Mineral oils have been looked upon with disfavor not only because they were used as adulterants of the more expensive oils mentioned, but because they did not give satisfactory emulsions with soap solution. A development which may have far-reaching effect is the utilization of mineral oils for fat-liquoring purposes in conjunction with sulphonated animal, vegetable, or fish oils, which are excellent emulsifying media and possess lubricating properties themselves.

A noteworthy addition to the mordants available for use upon chrome leather previous to dyeing with aniline colors was made a few years ago. An extract prepared from osage orange wood, introduced under the name of Aurantine, has found successful application as a substitute for fustic extract. The yellow coloring matter of the extract is readily absorbed by chrome leather and this preparation will probably be more extensively used when it is better known.

In the finishing operations, considerable ingenuity has been exercised in devising means of overcoming defects in the skins and improving the appearance of the leather. A process for finishing colored chrome leather which fairly effectively covers irregularities arising from uneven color adsorption in the dye bath, and tends to give a desirable even appearance, employs what are known as pigment finishes. These consist of very finely ground earth colors suspended in suitable gum or resin solutions, and can be applied in the same way as ordinary finishes. If the skin defects are very prominent, it may be necessary to buff the grain lightly on an emery or carborundum wheel to obtain an even bottom on which to apply the finish. The finishes are so constituted, and have such good covering property, that it is not always easy to decide without the aid of a microscope if the grain has actually been buffed.

Steady improvement in the quality of chrome leather has been made by the American tanner as the principles underlying the process have been better understood, and he has earned and maintained a well-deserved reputation for the character of his goods.

Certain grades of American glazed kid, for example, are recognized as standard articles and great care is exercised by the producers to maintain the uniformity and excellence of their products. Formerly black glazed kid was the sole product of the majority of goatskin tanneries, but in recent years, either to satisfy the demands of ladies' fashions or to create them, there has been a large output of colored goatskins in a great variety of very delicate shades. For the production of these leathers it is necessary to have raw skins of the very highest grade, free from natural and acquired defects. As several glazed kid tanneries in the Philadelphia district are each capable of producing over 1,000 dozen finished goatskins daily, it will be understood that it is possible to select a reasonable number of high-grade skins for the purpose mentioned. Large-scale operation is not confined to the class of leather mentioned, as very large tanneries are engaged in the production of calf and side leathers.

The Chicago packers, who control a large portion of the raw hides and skins of the country, have recently entered the chrome tanning business, and this may eventually lead to a still greater development of the industry of the future.

While progress has been made in the technique of leather manufacture, great advances have also been made in labor-saving machinery. On account of the high cost of labor, the American tanner has always been on the alert to obtain such machinery, and its design and manufacture have offered a good field for the engineer. It seems safe to assert that tanning machinery is developed to a greater extent in America than in any other country.

One must admire and respect the initiative, courage, and business ability of the American chrome tanners who founded and developed this most important industry. However, the industry cannot be regarded as exclusively American, as some of the most important advances have been made through the adoption of European ideas. It is well known that traditions and time-honored customs do not appeal strongly to the average American merely on account of their extreme age. This may be considered an asset where the manufacture of chrome leather is concerned, as it enabled the tanner to forsake methods which, though successfully applied to vegetable tanning throughout the centuries, may be totally unsuitable for chrome leather, and he has prospered by being progressive.

THE CHROME TANNING INDUSTRY IN GREAT BRITAIN.*

By M. C. Lamb.

The first attempt at the conversion of prepared hide into leather by a process of mineral tanning is generally credited to Professor F. L. Knapp, who obtained patent rights for the use of normal or basic salts of chromium, iron, manganese, etc., in combination with fatty acids for the purpose. Although in its original form this process was not applied commercially, owing to the fact that Knapp regarded his discovery as being applicable to the employment of iron salts rather than chrome salts and devoted his energies chiefly to the commercial application of these, the credit for the discovery of the fact that a basic salt of chromium possesses tanning properties is undoubtedly his.

The patent of Christian Heinzerling of 1878 was the first process of mineral tanning to be applied on a commercial scale. Heinzerling's method consisted of the application of a mixture of potash alum and potassium bichromate and the subsequent treatment of the hide with albuminous matter such as blood. About 1880, the Eglinton Chemical Company of Glasgow acquired the right of granting licenses to work Heinzerling's process in this country and commenced the manufacture of leather on a small scale at their Exhibition Tannery, Glebe Street, Glasgow. The process was worked only with a very limited degree of success. The chromic acid was very imperfectly reduced by the hide substance, and proteins and fats were used for subsequently impregnating the "leather," for the purpose of rendering it more water-resistant.

During the period when the Eglinton Chrome Tannery Company were endeavoring to pioneer this process, Professor J. J. Hummel, of the Yorkshire College, Leeds, was consulted with a view to devising a process for fixing the chrome salt on the fiber. After some experimenting, he suggested a method then used in the chrome-mordanting of wool and cotton, of applying chromic acid to the prepared hide and subsequently reducing this by treatment with sodium bisulphite or thiosulphate. Samples of leather were actually produced by this process, but for some reason, unknown to the author, the method was not worked on a commercial

* Reprinted from *J. S. C. I.*, **38**, 266T, (1919).

scale, though it anticipated the method patented by Augustus Schultz in America in 1884. Schultz's process was the first successful method practiced on a large commercial scale for the manufacture of pure chrome tanned leather, and with minor modifications is the process now being worked in this country for the tanning of goatskins for glacé kid.

In 1893, Martin Dennis took out patent rights in America for the use of a basic chromium chloride solution for tanning. The Martin Dennis process as regards the preparation of the chrome tanning liquor is very similar to that originally advocated by Knapp. This process was the commercial pioneer of the now common method of chrome tanning by what is termed the "single-bath" process, depending upon the utilization of a basic chromium sulphate or a basic chromium chloride solution.

The methods of Schultz and Martin Dennis were brought to the notice of the British leather trade by Professor H. R. Procter, who when visiting the Chicago Exhibition of 1895 had an opportunity of seeing the Schultz process being worked by Messrs. Burk Bros. and Robert Foederer, of Philadelphia. The process of Martin Dennis was also being experimented with by several American chrome tanners. These two methods of chrome tanning were brought directly under the notice of the members of the Leeds Leather Trades' Association at a public lecture given by Professor Procter on his return, and excited considerable interest. Several of the more important light leather manufacturers of Great Britain, seeing possibilities in this new tannage, commenced experimenting. The earliest of these were Messrs. J. J. Flitch & Sons, Leeds, who were rapidly followed by other manufacturers, among whom may be mentioned Messrs. R. Fawsitt & Sons, and East, Kinsey & East, of Bermondsey, and Ward & Co., of Worcester. These firms, who had previously been engaged in the manufacture of calf kid by the alum process, found that their experience in the preparation of the goods for the manufacture of leather by this older mineral tannage enabled them to make rapid headway as compared with the firms who were only familiar with the vegetable tanning process.

The patents of Schultz and Martin Dennis having both been anticipated in Great Britain, no attempt was made by the holders of these patents to contest the right of the British tanner to

manufacture without payment of royalties. Considerable difficulties were experienced by the early pioneers of chrome tanning, and much valuable raw material was wasted by reason of an imperfect knowledge of the chemistry of the process and the lack of knowledge how to prepare the pelt suitably before tanning. To those firms who had been chiefly interested in vegetable tanning the method of Martin Dennis appealed the more strongly of the two processes, owing to the fact that it was worked on somewhat similar lines to vegetable tanning, the prepared pelt being placed in a weak solution of the basic chromium chloride or chromium sulphate, and the strength of the solution being increased as the tannage progressed.

The progress of the application of this "single-bath" method of chrome tanning became more rapid after the publications of Procter in 1897 and 1898, in which he advocated, in the first place, the reduction of an acidified solution of potassium bichromate by organic reducing agents, *e. g.* glucose, sugar etc., following on somewhat similar lines to the method described by Hummel in the account of chromium mordants in his book entitled "The Dyeing of Textile Fabrics;" and a still more simple method of making a basic chrome liquor by the addition of an alkaline carbonate to a solution of chrome alum. This salt, which was obtainable in large quantities as a by-product in the manufacture of alizarin from anthracene, having very little commercial application, was available at a very low price. The liquor was more simply prepared than that patented by Martin Dennis and was more uniform than that obtained by the reduction of chromic acid with organic reducing agents. In consequence, this method of preparing chrome liquors was almost universally adopted and continued to be used up to 1914, when owing to the difficulty of obtaining chrome alum, tanners had of necessity to revert to the manufacture of chrome liquors by the reduction of chromic acid by reducing agents, glucose, farina, and starch being employed until the use of these materials was prohibited, when sodium bisulphite, sodium thiosulphate, and sulphurous acid were pressed into service.

The process of chrome tanning is, apparently, dependent upon the impregnating and covering of each individual fiber with a coating of a basic chromium salt or oxide, thus preventing the

fibers subsequently adhering when the leather is dried, and at the same time so protecting the fibers that the leather is capable of withstanding the action of boiling water and other hydrolyzing agents.

The principle of tanning by mineral agents consists, according to Stiasny, in the formation through hydrolysis of a colloidal basic constituent, which must possess a certain power of membranous diffusion to be of any practical tanning value.

One of the obstacles to progress in the manufacture of chrome leather in the early days of its introduction was the uncertainty which existed as to the chemical reactions which were involved. The reactions in the double-bath process of chrome tanning are complicated.

Eitner, in about 1905, after studying this process, proved that under certain conditions the reaction between the chromic acid and the acidified thiosulphate resulted in the production of a basic chromium sulphate, as shown by the following equation:

$$K_2Cr_2O_7 + 6HCl + 3Na_2S_2O_3 \rightleftarrows 2KCl + 4NaCl + Na_2SO_4 + 2Cr(OH)SO_4 + 2H_2O + 3S,$$

which is confirmatory of the statement that the tannage is due to the production of a basic salt.

In the tannage of hides for "box" leather, calf, etc., the single-bath process is universal in this country, and it is generally considered that a basicity between 85 and 95 ($Cr : SO_4 = 52 : 85$—95) is most suitable.

The method of carrying out the tannage is extremely simple. The goods are placed, preferably, in a drum with sufficient water to make a comfortable float. The pelts having been weighed are introduced, and the liquor is added in small quantities during the rotation of the drum in the earlier stages. The total quantity of liquor necessary, in terms of chromic acid, is between 3 per cent. and 4 per cent. on the pelt weight of goods processed, and this should be added in not less than four portions, as the tannage proceeds. The addition of 5 per cent. of either common salt or sodium sulphate is advisable. The goods are satisfactorily processed when it is found on making a test that the resulting leather will withstand immersion in boiling water without being detrimentally affected. The usual length of time required is about 6

hours, but in the case of thick goods, it is sometimes advisable to keep the goods in the solution for a longer period.

The double-bath process is used exclusively upon goatskins for glacé kid. The goods are drummed in a solution of 3-4 per cent. chromic acid and 3-4 per cent. salt, until thoroughly impregnated, and are then transferred to a solution of sodium thiosulphate, using 15-20 per cent. acidified with 5-7 per cent. of sulphuric acid, and drummed until the chromic acid is completely reduced to basic chromium sulphate, as indicated by the color of the leather.

It will be understood from what has been said that the difference between the single-bath process and the double-bath process (Schultz's) is that in the first mentioned the tannage is produced by the direct application of a basic salt to the pelt, whereas in the latter case the basic salt is produced on the hide fibers.

Sulphur, resulting from the decomposition of the sodium thiosulphate in the second bath of the double-bath process, is deposited in the interstices between the fibers in a colloidal form and acts as a lubricant to the fibers themselves, imparting a more supple feel to the leather. This deposition of sulphur is important from the point of view that it has been found that leather with a large sulphur content is capable of withstanding higher temperatures than leather containing smaller quantities. In certain instances it has been found advantageous to increase the sulphur deposit, particularly where the leather is to be used for motor tires and is to be subjected to the operation of vulcanization in conjunction with India rubber.

The treatment of chrome leather after tanning consists in neutralizing the acid liberated during the tanning process, removing the soluble salts from the leather, and, in the case of leather intended for boot uppers, fancy purposes, etc., the dyeing and fatliquoring operations.

The common method for neutralization is by the use of borax or alkali carbonates. Blacks are usually dyed by the use of logwood in conjunction with direct cotton dyestuffs, or acid and basic coal tar coloring matters, in which latter case the dyestuffs are applied after treatment with the logwood mordant.

In the dyeing of colored leathers, the leather is usually mordanted with a vegetable dyewood or tanning mordant, *e. g.* gam-

bier, fustic extract, etc., and then subsequently dyed either with basic coal tar colors or, what are generally preferred, acid wool colors.

The operation of fat-liquoring, which has for its object the lubrication of the fibers of the leather with a view to rendering it more soft and supple, consists of impregnating the leather with a dilute oil and soap emulsion. This consists, generally, of a mixture of either vegetable or animal oil in conjunction with soap, the latter being used chiefly as an emulsifying agent. The soap ingredient of the fat-liquor has, for the last two or three years, been largely replaced by sulphonated animal, vegetable, and mineral oils. The sulphonated oil acts as a carrier for the animal and vegetable oils in conjunction with which it is used, thereby effecting more complete penetration of the emulsion through the fibers and resulting in a better nourished and softer leather.

A few further special points of importance showing the progress that has been made in the manufacture of chrome leather in Great Britain may be mentioned.

It was found that, in the original formula of Schultz, consisting of 5 per cent. of potassium bichromate and 2½ per cent. commercial hydrochloric acid, only about two-thirds of the total quantity of bichromate is converted into chromic acid, and the unconverted bichromate is not absorbed and subsequently reduced. Considerable economy was affected by the use of a sufficient amount of acid in the first bath to effect the almost complete conversion of the bichromate into chromic acid. The quantities of thiosulphate (10 per cent.) and hydrochloric acid (5 per cent.) recommended by Schultz were found to be insufficient and were materially increased.

Whereas it was customary a few years ago to use a fresh solution of thiosulphate and acid for each pack of goods, it is now more general to use a standing bath; this has resulted in considerable economy and it is generally conceded that the finished leather is improved.

During the past few years great attention has been drawn to the importance of the degree of basicity of the chrome liquor when processing goods by the single-bath method, and to the necessity for adjustment of this for the particular class of goods being tanned.

The influence of the degree of basicity upon the resulting leather will be better understood when it is pointed out that whereas the normal salt is only absorbed to a very small extent by the pelt, a basic solution is readily absorbed, and consequently the more basic the solution the greater will be the deposition of chromium hydroxide on the fibers. When the chrome liquor is too basic, the tannage will be extremely slow, there will be a considerable liability of the production of "drawn grain," and a liability of over-tanning the grain surface with the consequent tendency to produce a brittle, "cracky," grained leather.

It has been found advisable to commence the tannage with a more acid liquor and to complete with a more basic liquor, and in this respect the process is comparable with the vegetable tanning process.

The chrome leather industry in Great Britain has attained very considerable importance. Whereas, prior to 1900, the bulk of the leather manufactured for the purpose of boot uppers was of vegetable origin, practically the whole of the leather used in the manufacture of the better quality boot uppers is now of pure chrome tannage. Chrome leather was used to the extent of 20 per cent. in the manufacture of boots for the Army during the recent campaign. Its behavior on active service was all that could be desired, and the only reason why a much larger amount was not employed was on account of the lack of tanning facilities.

Chrome-tanned sole leather is being made in very large quantities, and while there is still a considerable amount of public prejudice to be overcome and also this method of manufacture is not applicable to the tanning of sole leather from all classes of hides, it would appear probable that this method of tanning will further extend, as the wearing properties of chrome leather are greatly in advance of those of leather tanned with vegetable products, and the tanning process only occupies about one-fiftieth of the time necessary in the latter case.

It is somewhat curious that this method of tanning sole leather has not been practiced to any very large extent in America. One of the earliest objections to the employment of chrome leather for soleing boots, *viz.* the liability to cause slipping when in wear, particularly on wet pavements, has been almost entirely overcome by impregnating the leather with hard waxes. This has the effect

of still further waterproofing the leather and also enables it to pick up small particles of grit, and thus minimize the defect just mentioned.

This paper would be incomplete without reference to the very important industry which has arisen from the chrome tanning process, *viz.* the manufacture of semi-chrome leather. This leather is prepared by first removing a portion of the original vegetable tannage from an already tanned leather by means of a weak alkaline solution, and afterwards re-tanning with a basic chromium sulphate solution or a basic chromium chloride solution; the dyeing, fat-liquoring, and finishing operations are almost identical with those practiced on real chrome leather.

In the early part of 1898, when American box calf made by the chrome process was exported to this country in large quantities and tanners of calf kid and others were engaged in experimenting in the manufacture of chrome calf there was a consequent decline in the popularity of curried leathers, and the shoe leather currier, who had been primarily engaged in the dressing of vegetable tanned calfskins for boot-upper leather, began to fear that chrome tanning might eventually supplant the leather that he was then producing and that the major part of his vocation would be taken from him.

Experiments were made by several British firms in the direction of retanning vegetable tanned leather, with the object of imparting to it certain characteristics of chrome leather, and eventually a result was obtained which was sufficiently satisfactory for the process to be generally adopted by the majority of leather dressers catering for the boot-upper leather trade. It was found that this leather, no doubt due to the presence of the tanning mordant, was capable of absorbing a greater amount of chromic oxide than was commonly found to be present in a pure chrome tanned leather. Properly prepared, this leather has certain chrome characteristics as regards softness and ability to withstand the action of boiling water without becoming damaged. This process of manufacture has been used on a very considerable scale, particularly in connection with the manufacture of brown-colored calf and black side leather.

This method of manufacture is only common to Great Britain and France. So far as the author is aware it has not been em-

ployed to any extent in other countries. This is most probably accounted for by the fact that in America and Germany, unlike Great Britain and France, the manufacture of leather is carried through in one works from hair to finish, whereas in the two latter mentioned countries it is quite common practice for the manufacture to be divided, the tanner handing his product over to a currier or leather dresser to complete the manufacture.

The manufacture of semi-chrome leather is also particularly applicable to employment upon the large quantities of half-tanned vegetable leather imported from India, which is capable of being finished into a substitute for real chrome leather.

In conclusion, the author would like to make reference to, and express the great obligation of this branch of the leather industry to Professor Henry R. Procter, who has, since the inception of this form of mineral tannage, been associated with the methods of analytical control universally adopted by chemists specializing in this industry, and who is thus to a very considerable extent responsible for the scientific advancement of this method of producing leather.

DETERMINATION OF CALCIUM OXIDE IN LIME AND LIMESTONES; AND THE USE OF CALCIUM OXALATE AS A STANDARD FOR POTASSIUM PERMANGANATE.

By Ernest Little and Walter H. Beisler.

Received September 24, 1919.

The first chemical process made use of in the conversion of hide substance into leather is that of depilation. The most common depilant is, of course, lime, and no other chemical is used so extensively by the leather manufacturer. It is essential, therefore, that the available CaO in the lime be accurately known.

The method of analysis now generally used by leather chemists consists of shaking 1 gram of lime in a liter flask with about 950 cc. of hot water and allowing it to stand several hours with frequent shaking. When the solution is cold, it is made up to the mark with distilled water at 20° C., thoroughly shaken and allowed to settle. Fifty cubic centimeters of the clear solution are titrated with N/10 acid using phenolphthalein as an indicator, and the total alkalinity thus found is calculated as CaO.

It is evident that even small amounts of the more soluble hydroxides, as NaOH and KOH, in the lime will give results much higher than they should be, and hence indicate that the lime contains more available CaO than it really does. Procter recognizes this fact when he says, "Impure limes often show a higher alkalinity than pure ones, the impurities reacting with the lime and forming alkali hydrates which are much more soluble than lime." An attempt has been made to remove this possibility of error and to substitute a method which is accurate and sufficiently rapid to allow of its use in practical work.

Calcium is usually determined by precipitation as a sulphate, carbonate or oxalate. The precipitation as $CaSO_4$, as outlined by Stollberg,[1] is probably the least satisfactory method. The solubility of calcium sulphate is rather too high to allow of a quantitative precipitation. The solubility is much less, however, in an alcoholic solution. The precipitation as calcium carbonate or oxalate constitutes a better method. The oxalate method is preferable because calcium oxalate is more insoluble than calcium carbonate. Kohlraush and Rose,[2] have found by conductivity measurements that the solubility of calcium carbonate is 0.00013 mole per liter while the solubility of calcium oxalate is only 0.000038 molecule per liter. The calcium oxalate may be

1. Ignited at a low temperature and changed to calcium carbonate.
2. Ignited to constant weight with the blast lamp and weighed as calcium oxide.
3. Changed to calcium sulphate by treatment with sulphuric acid, and weighed as such.
4. Decomposed with hot dilute sulphuric acid and the liberated oxalic acid titrated with standard potassium permanganate.

The objection to the first method is that it is difficult even with the most delicate temperature regulation to change all the calcium oxalate to the carbonate without breaking some of it down into CaO. The objection to the second method of handling the calcium oxalate is that calcium oxide is very hygroscopic and during weighing takes on appreciable amounts of water and carbon dioxide. The third method might be satisfactory were it not for

[1] *Z. Angew. Chem.* **17**, 269.
[2] *Z. Physik. Chem.* **12**, 234 and **44**, 197.

the probable loss due to spattering during the heating to drive off the excess of sulphuric acid and the oxalic acid formed. The titration with permanganate is the best procedure being more accurate and quicker than the other methods.

The methods suggested for determining the available calcium oxide in lime is as follows. Treat a 1 gram sample with about 950 cc. of hot water in a liter graduated flask. Stopper the flask to prevent the carbon dioxide of the air from reacting with the calcium hydroxide and shake frequently to insure complete solution. After several hours, when the solution is cold, make up to the mark with distilled water at 20° C. Mix thoroughly and allow the residue to settle. Pipette 100 cc. of the clear solution into a beaker. Make acid with hydrochloric acid, add 5 cc. bromine water and boil to oxidize any ferrous iron to the ferric condition. Make the solution slightly alkaline with ammonium hydroxide, heat to boiling and add slowly, with constant stirring, about 10 per cent. more hot ammonium oxalate solution than is sufficient to cause complete precipitation. Heat on water bath for 20 minutes with occasional stirring. The calcium oxalate should settle to the bottom leaving a clear solution. After testing for complete precipitation, filter off the precipitate and wash with hot water until it is free from chlorides or until the washings fail to decolorize dilute permanganate, acidified with sulphuric acid. Punch a hole in the filter paper and wash the precipitate into the beaker in which the precipitation was made. Dilute to 150 cc. Place beaker under funnel and pour about 30 cc. of 1-3 sulphuric acid down the sides of the funnel and wash thoroughly with hot water to make sure that none of the oxalic acid is left on the paper. Heat the solution to about 80° C. and titrate slowly with standard potassium permanganate.

$$\text{cc. } \frac{N}{10}\ KMnO_4 \times \frac{CaO}{20{,}000} \times \frac{100}{\text{Wt. sample}} = \text{per cent. CaO.}$$

$$\text{or cc. } \frac{N}{10}\ KMnO_4 \times 0.0028 \times \frac{100}{0.1} = \text{per cent. CaO,}$$

$$\text{or cc. } \frac{N}{10}\ KMnO_4 \times 2.8 = \text{per cent. CaO.}$$

NOTES.

1. A slight excess of the precipitant is added, as is known, to reduce the $[Ca^{++}]$ remaining in solution to a minimum. This

In order to more clearly demonstrate the adaptability of the suggested method for the determination of "available CaO" and "total CaO" in lime, several samples were obtained from Newark tanneries. They were first analyzed for available calcium oxide, total calcium oxide, silica, iron and aluminum oxides and magnesium oxide, using the method of analysis as outlined by Procter. The available calcium oxide and total calcium were then determined by the suggested method. The results of analysis of three of the samples are given below.

Determination	Usual method per cent.	Proposed method per cent.
No. 1 Available CaO	78.80	78.75
Total CaO	81.54	81.66
SiO_2	1.68	
MgO	0.30	
$Fe_2O_3 + Al_2O_3$	0.75	
No. 2 Available CaO	80.32	80.27
Total CaO	82.63	82.71
SiO_2	3.64	
MgO	0.76	
$Fe_2O_3 + Al_2O_3$	0.27	
No. 3 Available CaO	75.45	65.40
Total CaO	78.89	78.96
SiO_2	1.62	
MgO	0.24	
$Fe_2O_3 + Al_2O_3$	0.50	

From these figures it is seen that, for Samples 1 and 2, the two methods agree very closely in the percentage of available calcium oxide obtained. This indicates that these samples are free from adulterants in the form of more soluble hydroxides, as sodium hydroxide. If such impurities were present, the available calcium oxide as determined by the alkalinity method would be much higher than the percentage obtained by the permanganate method. The data obtained for sample 3 would indicate the possible presence of NaOH in the sample.

Standardization of Potassium Permanganate.—Potassium permanganate is usually standardized against one of the following substances:

(*a*) Iron wire.
(*b*) Ferrous ammonium sulphate.
(*c*) Oxalic acid.
(*d*) FeO.
(*e*) Iron ore.
(*f*) Sodium Oxalate.

The use of iron wire is unsatisfactory due to the fact that it is impure and does not run uniform, thus making the use of a percentage purity factor unreliable. Mohr's salt can be obtained practically 100 per cent. pure and is quite a satisfactory standard. If it takes on moisture, however, it is difficult to dry without driving off some water of crystallization. Oxalic acid is also obtainable in very pure form, but upon drying it gives up some of its water of crystallization, and also decomposes into water, carbon dioxide and carbon monoxide at a temperature of 98°. Ferrous oxide and a standard iron ore are good standards. The method of standardization is longer, however, and the iron ore is not a primary standard as its iron content must first be accurately determined. Sodium oxalate (Sörensen) is the best standard for permanganate. It can be obtained very pure, contains no water of crystallization and can be dried at 100° C. with no decomposition. At the present time, however, it is rather expensive and difficult to obtain.

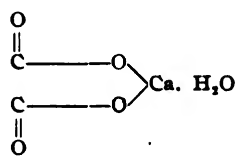
An attempt has been made to find another standard, which could be made in the laboratory and which would give accurate results. The use of calcium oxalate suggested itself, and experiments have shown that it is quite as satisfactory as sodium oxalate.

The calcium oxalate was prepared by dissolving C. P. calcium oxide in hydrochloric acid, neutralizing with ammonia and adding a slight excess of acetic acid. The calcium oxalate was then precipitated by the slow addition of ammonium oxalate to a large volume at boiling temperature. After prolonged heating on the water bath and washing the precipitate several times by decantation, the calcium oxalate was filtered on a Büchner funnel with suction, and thoroughly washed, first with dilute acetic acid and then with hot water. The washing with hot water was continued until the washings were free from chlorides and would not decolorize an acid solution of dilute permanganate. The oxalate was then air dried, finely powdered and put in a glass stoppered bottle. Under the conditions of the preparation, the calcium oxalate crystallizes with 1 molecule of water. Some difficulty was experienced in finding the proper temperature at which the $CaC_2O_4.H_2O$ could be dried in order to drive off all the mechanically held water, and leave a reasonably stable compound.

Ostwald[3] says "calcium oxalate holds varying amounts of water of crystallization depending upon the temperature. It should not be heated too hot, otherwise it will decompose to calcium carbonate and carbon monoxide, and at red heat to calcium oxide."

Abegg[4] says "calcium oxalate loses all its water of crystallization at 200° C. At glowing temperature it decomposes to calcium carbonate and carbon monoxide."

Fresenius[5] says "calcium oxalate is unaltered in air or at 100° C. Dried at 100° C. it invariably has the following composition:



CaO —	38.36%
C_2O_3 —	49.32%
H_2O —	12.32%
	100.00%

At 205° C. calcium oxalate loses its water of crystallization without decomposition. At a somewhat higher temperature, still not reaching dull redness, the anhydrous salt is decomposed to calcium carbonate and carbon monoxide."

In the laboratory the calcium oxalate was dried at temperatures ranging from 80° C. to over 200° C. Potassium permanganate, previously standardized against Sörensen's sodium oxalate, was then standardized against these samples of calcium oxalate and the results compared. It was found that when calcium oxalate is dried to constant weight at 140° C. it gives results quite as good as those obtained with Sörensen's sodium oxalate, and the salt is sufficiently stable to warrant its use as a standard. Temperatures below 140° C. were less satisfactory and when dried at temperatures above 150° C. the last molecule of water is gradually driven off. It has also been noted that when the oxalate is dried to constant weight at 140° C. and then exposed to the air for several days, it can be dried at 110° C. after which it may be used as a standard.

Standardization of potassium permanganate with pure calcium oxalate and with Sörensen sodium oxalate.

[3] "Grundlinien der Anorganischen Chemie," p. 535-6.

[4] Handbuch der Anorganischen Chemie, II 2., pp. 162-163.

[5] Quantitative Chemical Analysis, pp. 145-146.

Drying temperature.	Formula	Gms. Sample	Cc. N/10 $KMnO_4$	Normality Calcium Oxalate	Normality Sodium Oxalate	Error
140° C.	$CaC_2O_4.H_2O$	.1500 gm.	20.95	0.0981	0.0982	—0.0001
"	"	"	20.95	0.0981	0.0982	—0.0001
"	"	"	20.90	0.0983	0.0982	+0.0001
"	"	"	20.95	0.0981	0.0982	—0.0001
"	"	"	20.90	0.0983	0.0982	+0.0001
150° C.	"	"	20.95	0.0981	"	—0.0001
"	"	"	20.80	0.0988	"	+0,0006
"	"	"	21.05	0.0977	"	—0.0005
"	"	"	20.95	0.0981	"	—0.0001
"	"	"	21.05	0.0977	"	—0.0005
"	"	"	20.90	0.0983	"	+0.0001
"	"	"	20.95	0.0981	"	—0.0001
"	"	"	20.90	0.0983	"	+0.0001
Dried at 140° C. and left in desiccator 24 hours.						
	"	"	20.85	0.0985	"	+0.0003
	"	"	20.85	0.0985	"	+0.0003
Sample was exposed to air several days, and then dried at 110° C.						
	"	"	21.05	0.0977	0.0977	0.0000
	"	"	21.10	0.0975	"	—0.0002
	"	"	21.00	0.0979	"	+0.0002
	"	"	20.95	0.0981	"	+0.0004

It has been pointed out that the alkalinity method, now in general use by leather chemists, for determining available lime is subject to inaccuracy in the presence of the more soluble alkalies and, therefore, cannot be depended upon to give reliable information. The proposed method for determining available calcium oxide is not affected in the least by these adulterants or impurities. Oxidizable matter is the only thing that might introduce an error and this is destroyed in the preliminary procedure. The permanganate method is somewhat longer and requires a little more manipulative skill than the alkalinity method, but the greater accuracy obtained more than outweighs this objection.

As calcium oxalate can be prepared in any analytical laboratory, its use as a standard for permanganate should be of interest to the leather chemist. It can be depended upon to give accurate results if properly prepared and carefully dried.

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ONE BATH CHROME LIQUORS AND THEIR ANALYSIS.

By William Klaber.

Received September 25, 1919

Commercial one bath chrome tanning liquors are produced by variations of the three general methods of rendering chrome alum basic, reducing bichromate with sulphur dioxide, bisulphites, hyposulphite and acid, etc., and reducing bichromate with organic reducing substances. Various additional chemicals may be added, such as aluminium, iron, and sodium salts. In the case of liquors produced by reduction with organic substances, the acidity as determined by titration with standard NaOH will be found to exceed the amount expected from the relative amounts of bichromate and acid used. The explanation is that organic acids are formed to which phenolphthalein is sensitive. No methods of analysis hitherto published seem to take this fact into account or to furnish any means of measuring the extent of this acidity.

The object of this paper is to suggest modifications of the recently proposed change of the Provisional Method for the Analysis of One Bath Chrome Liquors[1], so as to include a mode of expression of this organic acidity, and to give a method of analysis which it is hoped may serve as the basis of an official method for the A. L. C. A.

The method outlined below has been in use for a number of years and has given satisfactory results. The principles and operations of the analysis are too well known to require detailed description. No specific method could cover the determination of all conceivable anions and cations which might be present, and therefore, it will be assumed that there are present Cr_2O_3, Al_2O_3, Fe_2O_3, Na_2O, SO_3, Cl, and organic acids, all or some of which are present in commercial one bath liquors.

For concentrated liquors, pipette 50 cc. into a 500 cc. flask, dilute to the mark, and take 50 cc. portions for analysis. For dry tannages, dissolve 5 grains in boiling water and dilute similarly. Very basic liquors are hydrolyzed and precipitate basic chromium salts at this dilution; in such cases it is necessary to prepare two solutions for analysis. For the determination of Cr_2O_3, Fe_2O_3, total acidity, total SO_3 and total R_2O_3, add 25 grains of NaCl to the sample diluted for analysis; for total Cl

[1] This JOURNAL, 14, 235.

and total Na_2O, add H_2SO_4. For dry products, express figures in terms of per cent. for liquors, in terms of grams per liter.

Portion No. 1. Cr_2O_3 and Fe_2O_3.

Oxidize with Na_2O_2, boil to decompose the excess peroxide, filter.

Filtrate: Determine Cr_2O_3 by acidifying, adding KI, and titrating with N/10 hypo, starch indicator.

Precipitate: Dissolve in HCl, and determine Fe_2O_3 by $KMnO_4$, $K_2Cr_2O_7$, or gravimetrically.

Portion No. 2. Total Acidity.

Titrate boiling solution with N/10 NaOH, phenolphthalein indicator.

Portion No. 3. Total SO_3 and Total R_2O_3.

Precipitate R_2O_3 elements with NH_4Cl and NH_4OH, filter and wash, redissolve precipitate with HCl, reprecipitate as before.

Precipitate: Ignite and weigh as Cr_2O_3, Fe_2O_3, Al_2O_3.

Combined Filtrates: Acidify with HCl, precipitate SO_3 as $BaSO_4$.

Portion No. 4. Total Cl.

Repeat operations of Portion No. 3, substituting $(NH_4)_2SO_4$ for NH_4CL, and H_2SO_4 for HCl. Combine filtrates and determine Cl by titration with N/10 $AgNO_3$.

Portion No. 5. Total Na_2O.

Repeat operations of Portion No. 3, combine filtrates, evaporate with excess of HNO_3, drive off NH_4 salts; moisten residue with H_2SO_4, ignite to constant weight, weigh as Na_2SO_4. Calculate to Na_2O.

Calculations.

Total Relative Acidity: Divide the number of cubic centimeters of N/10 NaOH used in Portion No. 2 by 1/6 the number of cubic centimeters of N/10 hypo used for the determination of Cr_2O_3 in Portion No. 1. This gives directly the ratio of gram molecular weights of monobasic acid to gram molecular weights of chromic oxide.

Acid SO_3: From the results of Portions No. 4 and No. 5, calculate the amount of SO_3 combined with Na_2O as Na_2SO_4; deduct this from the total SO_3 as found in Portion No. 3. The difference is acid SO_3.

Organic Acidity: This is derived by the following formula:

$$\text{Organic Acidity} = \text{total relative acidity} - \frac{\frac{\text{Acid } SO_3}{40.03}}{\frac{\text{Total } Cr_2O_3}{152.2}}$$

This figure expresses a measure of the organic acids in terms of gram molecular weights of monobasic acid relative to 1 gram molecular weight of Cr_2O_3.

Al_2O_3: Total R_2O_3 — Cr_2O_3 and Fe_2O_3.

Acidity of Cr_2O_3: Al_2O_3 and Fe_2O_3 are considered to be present as the normal sulphates and the SO_3 calculated to be so combined is subtracted from the acid SO_3. The difference is the SO_3 combined with Cr_2O_3. In conformity with the method adopted in expressing the total acidity, the ratio of this acidity to Cr_2O_3 is derived in terms of gram molecular weights of monobasic acid to 1 gram molecular weight of chromic oxide by the following formula:

$$\frac{\frac{SO_3 \text{ combined with } Cr_2O_3}{40.03}}{\frac{\text{Total} Cr_2O_3}{152.2}}$$

The following results were obtained from the analysis of a one bath tannage in powder form.

	Per cent.	
Cr_2O_3	23.70	used 46.72 cc. N/10 Hypo
Total acidity		" 33.9 cc. N/10 NaOH
Total SO_3	37.05	
Total R_2O_3	26.54	
Fe_2O_3	None	
Cl	None	
Na_2O	14.71	

Calculations

$$\text{Total relative acidity} = \frac{46.72}{\frac{33.9}{6}} = 4.35$$

Acid SO_3:—

Total SO_3	37.05%
SO_3 combined with Na_2O	18.96%
Acid SO_3	18.09%

all conceivable anions and cathions which might be present, and,

Organic acidity :—

$$4.35 - \frac{\frac{18.09}{40.03}}{\frac{23.7}{152.2}} = 1.45$$

Al_2O_3 .... 2.84%

Acidity of Cr_2O_3 :—

Acid SO_3	18.09%
SO_3 combined with Al_2O_3	6.67%
SO_3 " " Cr_2O_3	11.42%

Relative acidity of Cr_2O_3 :—

$$\frac{\frac{11.42}{40.03}}{\frac{23.7}{152.2}} = 1.83$$

The product under examination is thus shown to consist of a basic chromium sulphate approximating $Cr_2(OH)_4SO_4$, sulphate of alumina, sodium sulphate, and organic acids.

The points which it was desired to bring out have been illustrated in the foregoing method and calculation of analysis. It is quite evident that no method of analysis which does not provide for differentiation between an expression of the various forms of acidity, can be satisfactory. The object of an analysis of this sort is to determine what one is handling; the one bath liquor analyzed was made from bichromate or chromate of soda, an amount of sulphuric acid used sufficient to produce a definite degree of chromium sulphate acidity, the mixture reduced with organic material, incidentally sulphate of alumina added and organic acids generated in the course of the reaction. For the purpose of more clearly expressing these and similar facts, it is recommended.

1. That the total relative acidity as determined by titration and calculation be considered as a method to be applied only to control work. For this purpose, it is admirable, depending as it does upon two simple titrations; in a complete analysis, it is merely a stepping stone.

2. That where Al_2O_3 and Fe_2O_3 are present, they be considered to exist as normal salts.

3. That organic acidity be determined in the manner shown and that it be expressed as the ratio of gram molecular weights of monobasic acid to gram molecular weights of chromic oxide.

4. That the ratio of gram molecular weights of monobasic inorganic acid combined with Cr_2O_3 to the gram molecular weights of Cr_2O_3 replace the present "Basicity" determination of the provisional method. The advantage of this mode of expression over that of Mr. J. A. Wilson's proposed standard method is that this ratio is the number of (OH) groups of $Cr_2(OH)_6$ replaced by acid radicals. Thus $Cr_2(SO_4)_3$ would have a value of 6; $Cr_2(OH)_3Cl_3$, 3; $Cr_2(OH)_2(SO_4)_2$, 4; etc.

ABSTRACTS.

Indian Industries. HIDES AND SKINS. *J. R. S. A.* 67, 646. There are, it has been calculated, about 180,000,000 cattle and 87,000,000 sheep and goats in India. How large is the quantity of hides and skins available for commercial use may, to some extent, be estimated by one fact Sir Henry Ledgard mentioned in the interesting paper he read before the Society last year.* Taking the figures for 1913, he showed that the total value of India's whole exports was £162 millions sterling, of which six commodities accounted for £142 millions, hides and skins being fifth in the list. In the admirable article which forms Appendix D of the Indian Industrial Commission's Report the position and prospects of this important trade are exhaustively discussed.

The United Kingdom has always taken the bulk of the tanned or dressed hides and a very large proportion of the tanned or dressed skins, while the raw material has gone to those countries which protected their manufacturers by the imposition of heavy duties on all but raw products. Till the war broke out, Germany, Austria, and Italy were the principal destinations to which raw hides were sent, and roughly three-fourths of the raw skins were purchased by the United States. Very little information is available regarding the internal consumption of hides and skins. Probably half the hides and nine-tenths of the skins available in the country are exported.

The export trade has, from the beginning, steadily expanded both in volume and value, and even more rapidly in value than in volume. Indian raw material fills an exceedingly important place in the leather markets of the world. Prices have constantly tended to rise, and important changes have thereby been brought about in respect of the internal consumption of leather.

This increase in the value of the raw material has naturally affected rural economy to some extent by stimulating the improvement of the organization for collecting hides and skins. Formerly, they were the perquisite of the village *chuckler* or *chamar,* who tanned them in a primitive way and supplied the needs of the villagers in the matter of leather.

* "The Indian Hide and Leather Trade," *Journal of the Royal Society of Arts,* Vol. LXVI, p. 274. Abst. This J. 13, 218 (1918).

The increased value of the hides and the ease with which they can be marketed have led the *chuckler*, in many places, to abandon the tanning business and to sell the hides to dealers for cash. It has also led the villager to dispute the *chuckler's* right to the hides, and to employ him instead as an intermediary in the disposal of them; while he now purchases leather in the open market from the agents or middlemen of the organized tanneries and hands it over to a *chuckler* to make up into whatever he needs.

Indian hides differ a good deal in size according to locality and breed; speaking generally, the larger hides come from the Punjab, the north of the United Provinces, and parts of Bombay and Madras. The inferiority of Indian hides is only partly due to the poor quality of the cattle. Branding depreciates their value enormously, and, as many of the cattle are used for draught work, their hides show signs of wear and tear. Only in the large towns, and more especially in the cantonments, are cattle killed for food, and the bulk of the hides available are those taken off animals which have died from disease, old age, or injury. Hindus are very averse from killing animals, and they allow their cattle to linger on in sickness and old age. The animals suffer and naturally their hides deteriorate, but the most fruitful source of injury is the merciless way in which cattle are branded. This is carried on to such an extreme that many thousands of hides are absolutely ruined, and large numbers of them are depreciated 50 per cent. in value through branding, which is done to satisfy the owner's esthetic eye or calm his troubled mind. It is supposed to be efficacious in keeping away evil spirits and preventing disease, and it is also largely practiced as a remedy for many diseases, especially in the nature of staggers or fits.

The prejudice against killing cattle is, however, disregarded in some parts of the country. In the Central Provinces and the United Provinces, "jerked" meat for export to Burma is prepared on a large scale, and there are a number of slaughter-houses at Agra, Damoh, Rahatgarh, Khurai, and other places, where thousands of cattle are slaughtered every day, and a trade not very dissimilar from that of the meat packers of Chicago is carried on. These establishments furnish large numbers of hides of a quality somewhat superior to those taken from the animals that die from natural causes, though the animals sent there for slaughter are usually past work.

The term "skins" is technically applied only to pelts of sheep and goats. Goatskins are larger, heavier, and of much better texture than sheepskins. Unlike hides, the majority of skins are derived from animals which have been slaughtered for food, and the pelts are, therefore, in a much better condition, and will compare favorably with similar classes of skins from other parts of the world. The tanning of skins is practically confined to Bombay and Madras, and the bulk of the business is done in the latter Presidency, the tanners of which supplement the local supplies by importing largely from other parts of India. The quality of skins varies very much with the season of the year; but, unlike hides, they are

generally at their worst during the rainy season, when the animals become feverish through exposure, and the effect shows in the pelts. The hair or wool grows longer on account of the cold, and this leads to loss of tissue, with the result that the pelt is thin and papery. The majority of the dried skins are exported to be chrome tanned in America or Europe and converted into glacé kid. Skins tanned by the chrome process do not gain substance like those prepared by vegetable tanning, and plump well-nurtured skins are, therefore, in great demand by chrome tanners.

It is difficult to obtain information regarding the tanning of leather in India before the industry came under the influence of Western methods. Judging by what is now done in remote districts, where the village tanner is still uninfluenced by modern methods of procedure, it is probable that the indigenous industry was in an extremely primitive condition and that only very inferior kinds of leather were produced. Tanneries of considerable size must have existed to supply the harness and saddlery for the enormous numbers of troops and retainers who were kept under arms by the numerous rajas, zemindars, and petty chieftains, who formerly exercised more or less independent sovereign powers throughout the country. The requirements of the town population were probably small and confined chiefly to sandals and vessels for holding oil and ghee; but the ryots used large quantities of village-tanned leather for water bags, for leather thongs, and for ropes.

European methods of tanning hides were first introduced by the military authorities to manufacture superior leather suitable for harness and other military accoutrements. Contemporaneously in the early forties of last century, a French Eurasian of Pondicherry, named D'Souza, introduced improvements in the native methods of preparing skins. He is said to have visited the island of Mauritius and to have there acquired a practical knowledge of the French processes of tanning and, on his return to Pondicherry, he started a tannery and, a little later, came to Madras and set up several small tanneries in the neighborhood of that city, the products of which were probably exported to England. Of his improvements the most important was the immersion of the tanned skins in a bath of myrobalans after the ordinary tanning had been completed. This prevents a very objectionable change in color which otherwise takes place on the exposure to sunlight of leather or skins tanned with *avaram* bark. There is no clear evidence that from his time till the advent of chrome tanning any further changes in the methods of tanning skins have been introduced into India. The small demand for highly finished skins in India was met by importation from Europe, and the somewhat crudely prepared Indian-dressed skins were welcomed by the tanners in Europe as the raw material from which to prepare the very best classes of light leather.

The developments of leather manufacture in contradistinction to the light tannages of Madras and Bombay are almost entirely the outcome of military efforts to obtain suitable supplies for boots and accoutrements. Where arsenals were established, tanneries usually followed.

In Europe and America machinery is very largely employed in tanneries and leather-working factories, but, although it has been employed on a considerable scale in the Cawnpore and Sion factories, elsewhere, till quite recently, it was conspicuous by its absence in the Indian tanneries, which produced the whole of the half-tanned leather and skins that bulk largely in the export trade of the country.

The action of various chemicals on hide substance has been the subject of scientific investigation for many years past, and, about 1895, the method of producing leather by means of chromium salts was thoroughly established in America on a commercial basis. The process was also taken up on the Continent and, somewhat more slowly and at a rather later date, by English tanners. Some experiments were made in India both in Cawnpore and Madras; but they resulted in nothing practical till, in 1903, the proposal was made in Madras to use leather prepared by this process for water bags for the country *mhots*. The experiments proved successful and resulted in the establishment of a Government factory, in which chrome leather was manufactured on a considerable scale and applied to a variety of purposes in place of bark-tanned leather. That this factory was prematurely closed there seems to be no doubt, as the progress of chrome tanning in India has been much slower than it is reasonable to anticipate would have been the case had Government assistance in pioneering the industry been given for a longer period. The developments have followed the line of least resistance, and, in the hands of private individuals, immediate profit has naturally been of greater importance than ultimate development. Of the chrome tanneries which were started, seven or eight have survived the initial difficulties, and are now mainly employed on the manufacture of leather for sandals and boots and shoes. The manufacture of black and brown box sides has been developed on a considerable scale, and this completely finished leather has found a profitable market in Great Britain.

At the outset it was thought that there would be a very large market for chrome leather for water bags, but progress in this direction has been comparatively slow. The rise in the price of leather has led the ryots to use light iron buckets, and competition with them left comparatively little profit to the chrome tanner. The Madras tannery was the first in the south of India to introduce the use of machinery in the tanning processes, and the success with which such machinery has been working has led to its adoption to some extent in bark tanneries. This latter development is a matter of some importance, as it has engendered a more progressive attitude among the Indian tanners.

Evidence of this is visible in the success which has attended the efforts of the Indian Munitions Board to stimulate the manufacture in India of certain classes of leather goods previously imported from abroad. The scrutiny of applications for priority drew attention to the possible market for locally manufactured roller skins, picker bands, leather belting, and raw hide pickers. Early in June, 1917, the Board accordingly informed Indian firms that if they could satisfy it, by production of suitable samples,

that these articles could be made in India, priority applications for import from abroad would be refused. A number of the more recently established tanneries of the improved type took the matter up with most encouraging results, and, with regard to roller skins and picker bands, it is understood that they have no difficulty in disposing of their outturn. The manufacture of leather belting and of raw hide pickers proved a matter of greater difficulty, and experiments are still in progress. Excellent belting has been made from specially selected hides, but the general average is not yet up to the required standard. In regard to pickers, the large sizes used on jute looms are working satisfactorily, but the smaller pickers for cotton looms still leave much to be desired.

The highest developments of manufacture at the outbreak of war were to be found in factories most intimately associated with the supply of material for military purposes and in the smaller tanneries devoted to the production of chrome leather. The bulk of the leather made in the country was either for internal consumption and of inferior quality or for export as half-tanned leather, to which the trade applied the term "East India Kips." Practically, the export trade was confined to Madras and Bombay, and was chiefly to Great Britain and, to a much smaller extent, to the United States of America and to Japan.

Some time after the outbreak of war, the value of the "East India Kips" as upper leather for army boots was realized in England, and efforts were made to increase and regulate the supply. From August, 1916, the Indian Government, at the request of the War Office, assumed complete control of the trade, and took over from the tanners the whole of their output. The arrangements made by the Commerce and Industry Department were transferred to the Indian Munitions Board, after its creation in March, 1917. In pre-war years the exports were below 200,000 hundredweight, of a value of less than two crores of rupees. In the year 1917-18 they reached 360,000 hundredweight, of a value approaching five crores of rupees. Roughly, in four years, the output of the Indian tanneries for this class of leather only has been doubled. The control of the trade has enabled some minor, but very important, improvements to be effected, the chief of which are the prevention of adulteration and the elimination of faulty flaying.

The problem of the future is how to obtain for India a larger share in the work of preparing her abundant raw material for the market. The limits of reference preclude any discussion of the tariff question and, though the trade has been, and will continue to be, affected by whatever fiscal policy is adopted, it is assumed that if sufficiently good finished material be produced, it will be possible to sell it at profitable prices.

There is a very large, but limited, supply of Indian hides, which was not sufficient to meet the demands made upon it in pre-war times, and it may be confidently anticipated that these demands will increase owing to the diminution in the number of cattle in the belligerent countries. It seems certain, therefore, that for a long time to come there will be a very serious shortage of hides and leather. For India to obtain advantage

from the situation it is necessary for her to make as good a leather from the local hides as can be made from the same hides elsewhere. The production of an inferior quality of leather will involve heavy loss, as it will only fetch a low price in competition with good leather made from similar material. There must, therefore, be no waste in this direction.

While the best Indian raw hides are distinctly inferior to the best produced under more favorable conditions in temperate climates, the Indian goatskins are of high grade and suited for first-class work. But from these skins Indian tanners have not so far been able to produce finished goods of anything like the quality that can be manufactured from them in Europe and America. In explanation of this, it has been alleged that in India it is too hot to produce first-class work, and there is no doubt whatever that the high temperature of the soaks and lime pits is a disadvantage. Tanning under tropical conditions has never been carefully studied by experts with both a scientific and practical knowledge of the trade. It may almost be accepted as axiomatic that the development of the Indian leather trade can only be accomplished by bringing to its assistance technically trained men, qualified to deal with the local problems and capable of modifying European and American methods to suit local conditions.

It is obvious that India cannot afford to neglect any of the advantages enjoyed by the tanning trade in other countries, and it may be regarded as essential that adequate provision should be made, as early as possible, for the investigation of tanning methods in India.

Hitherto the Indian trade has been run by *mistris* possessed of much practical experience, but absolutely ignorant of the most elementary knowledge of the principles underlying their practice. It is generally recognized that this can no longer continue, and that if India is to gain the position in the leather world to which she is entitled by reason of the abundance of raw material at her command, the tanning and leather industries must pass under the control of expert technologists, and scientific methods must replace empirical and rule-of-thumb working.

The inferior quality of Indian products is also due to the inferior skill and knowledge of the Indian workmen, especially in respect of the finishing of leathers. Outside the factories engaged on military work, and outside the few small ones which have sprung up as a result of the Madras efforts to introduce chrome tanning, neither currying nor finishing leather is understood or practiced, and whatever work is necessary in this direction is undertaken by the Indian *chuckler,* as a preliminary to the actual work of making the article which he has in hand. This can be remedied in the demonstration factories if skilled workmen are obtained from Europe to act as instructors.

The imports of finished leather and of goods made from leather are not unimportant, but many of them are the products of specialized factories, which it will not pay to establish in India till the demand is very much greater than it is at the present time.

The internal consumption of Indian-made leather is by no means accurately known. There are few parts of the country in which the village tanner does not still exist, and there are many small local tanneries of a slightly improved character in the south of India from which the agricultural population gets what it wants.

By far the most important item for which leather is required in India is the water bag by which water is lifted from millions of wells for the irrigation of the fields. To an appreciable extent, in recent years, iron buckets have replaced leather, and efforts are now being made to introduce cheaper fabrics made from vegetable fibers. It is not improbable that the use of leather for this purpose will steadily decrease, and, if such be the case, it will increase the visible supplies of hides on the market.

The Indian demand for boots and shoes and sandals is on the increase; but it is small as yet compared with the vast population. That it will grow in the future is a certainty, and it is likely that for boot uppers and sandals chrome leather will be very largely used. Chrome sole leather has been extensively tried and has proved extremely durable, and, in a country where pavements do not exist, the objection that it is slippery in wet weather has not the force which has practically precluded its use for footwear elsewhere.

The Indian tanning trade must, therefore, look to foreign markets for the sale of its products, and the quantity of raw material is so enormous that it will ultimately need very many large establishments to deal with it, and a high degree of specialization seems at least possible.

There is not the smallest doubt that foreign countries will endeavor to secure the Indian raw material and to refuse Indian-manufactured leather, as in the past. Assuming, however, that they cannot get the former, they will undoubtedly accept the latter. Future developments must to a large extent depend upon the work done in the experimental factories which have been recommended; but already sufficient experience has been accumulated to show that it is possible to export from India finished leather which meets with a ready market in the United Kingdom.

The article ends by concisely stating the conclusions the Commission have reached. India produces a very large, but not definitely ascertained, number of hides and skins which are accounted for under the following heads: (1) Those wasted in rural areas by the carelessness of the local *chucklers*, or owing to the fact that the hides themselves have become valueless; (2) those made into inferior leather by the village tanners; (3) those made into a good class of finished leather by modern tanneries; (4) those half or lightly tanned and exported; (5) those exported as raw hides; (6) those exported as finished leather, and chiefly as chrome box sides. So far these exports have been insignificant in volume, but they are of great importance as indicating future possibilities.

There seems to be little doubt that after the war new tanneries will be started to produce finished leather for export, and their fate will largely depend upon the quality of the leather which they turn out. Here Government can render valuable assistance by assuming to a large extent

responsibility for the technological investigations which have been indicated. Success will result in an improvement of the industry all along the line, beginning with a decrease of waste in rural areas and the diversion of the hides used by the village tanners to modern tanneries, in which a better class of leather will be produced. There will obviously be an increase in the amount of visible raw material; but whether this will be sufficient to meet the growing requirements of the country is a matter on which no definite opinion can be expressed. The general improvement of the technique in tanning will lead to an increase in the exports of finished leather and to a corresponding decrease in the exports of hides. The extent to which exports of finished leather will grow will depend upon the demand from foreign markets not closed by tariffs, and on the extent to which protected markets can be forced to accept leather made in India. Judging by the very great value of the imports of leather into Great Britain from the Continent and from America in the years immediately preceding the war, there is obviously a very important market open to Indian tanners if they can manufacture material of sufficiently good quality. Access to the protected markets is a matter of less certainty; but there are powerful means which will doubtless be used to insure it. The position of the manufacturer of half or lightly-tanned leathers is less assured. He should be prepared to meet the contingency of a possible decrease in the demand for his products; and this he can best face by being in a position, if necessary, to direct his energies to the production of chrome leathers.

Swedish Decree Against "Loading of Leather." *Commerce Reports*, Oct. 6, 1919. A decree of April 11, 1919, provides against the use of certain tanning substances when intended to increase the weight of leather. The provisions of the decree follow:

(1) Sole and strap leather may not be made heavier with substances which are not necessary for tanning or for further preparation of the leather. Neither may tanning substances be used with intention to increase the weight of such leather. Barium, magnesium, lead and tin salts, and other mineral salts, also glucose, dextrine, melass, and similar organic substances may be used only in very small quantities for bleaching and preparing the leather mentioned above.

(2) Increased weight according to Article 1 exists when the quantity of non-organic substances found in the ashes of the leather exceeds 3 per cent. in whole and half hides, middle pieces, and separated front pieces; 3½ per cent. in bellies, or if the loss of organic and inorganic substances through cleaning exceeds 20 per cent. in whole and half hides, middle pieces, and 25 per cent. of the weight of the air-dried leather in bellies. Air-dried leather shall be calculated to contain 18 per cent. water. Examination for discovering whether increased weight exists shall be made by the technical high school institute for testing material. The Commerce Kollegium has the right to issue further directions concerning this examination.

(3) Sole or strap leather imported to the country may not be delivered by the customshouse if on examination it is found that the leather is made heavier, according to Article 2. Such leather may, if according to the customs regulations the leather has not been unlawfully imported, again be exported. If such export has not taken place within four months, the goods will become the property of the Government.

(4) It is the duty of the leather manufacturer to supply each piece of different kinds of leather mentioned in Article 1 with a clear and durable stamp, including the word "Imported" and the importer's name or registered trade mark.

Sheep and Goat Raising in Brazil. *Commerce Reports,* Sept. 23, 1919. The principal sheep-raising States are Sao Paulo, Rio Grande do Sul, and Minas Geraes, where the breeding has received considerable attention. The breeds thus far introduced are: Southdown, Romney, Marah, Hampshire Down, Oxford Down, Merino, Turco, Lincoln, Rambouillet, etc. The State which appears to be best fitted for sheep raising is Rio Grande do Sul, where the Southdown, more commonly known as the *cara negra* (black face), is preferred owing to the facility with which it adapts itself to climatic and pastoral conditions there.

In Sao Paulo, as well as in Parana and Santa Catharina, much attention is being given to the intensive raising of superior races of sheep known only a few years in this country. It is believed that on the plains of the northern part of Rio Grande do Sul, Santa Catharina, and Parana at an altitude of 600 meters or more above sea level, the temperature and other conditions are more favorable than the same latitudes of Australia and the Republics of Argentina and Uraguay. Taking into consideration the weight and quality of wool, it is believed that in time under proper development the sheep in this section of the country will compete very favorably in the world markets with those of New Zealand and the River Plate.

While sheep raising requires more attention than cattle raising, sheep acclimate themselves more easily to the Brazilian plains than cattle do. However, with proper care given to pastures, corrals, the elimination of insect pests, etc., it is believed that an important industry may be developed along these lines, especially in the furnishing of raw wool to the Brazilian textile factories.

As will be seen by the following statistics, Brazil occupies second place among the goat-breeding countries of the world: South Africa, 11,520,744; Brazil, 6,919,550; Argentina, 3,945,986; Algeria, 3,772,424; Germany, 3,438,290; Spain, 3,116,238; Austria-Hungary, 3,014,190; Italy, 2,714,828; Bulgaria, 1,459,344; France, 1,230,238; Portugal, 1,034,218; Serbia, 630,579; Tunis, 499,164; Switzerland, 358,093; Chile, 288,056; Norway, 240,303; Netherlands, 232,478; Belgium, 217,823; Japan, 89,488; Sweden, 71,054; and Uruguay, 19,951.

In 1916 the Brazil herd counted 7,204,920 head of sheep. Of this number there were in Bahia 1,841,900 head; in Ceara, 320,950; in Pernam-

buco, 356,520; in Piauhy, 256,060; in Rio Grande do Norte, 207,510; in Rio Grande do Sul, 2,622,920. The remainder was distributed throughout Brazil.

On February 27, 1918, a decree was promulgated by the President to aid the breeding of sheep and goats in Brazil. It provided for the payment of certain premiums to municipalities, agricultural societies, zootechnic posts, etc., engaged in this branch of stock raising when specific regulations concerning the condition of the land, the use of modern appliances, the kind of stock imported, etc., had been complied with.

Progress in Tanning Fish Leather. Bureau of Fisheries, *Commerce Reports,* Sept. 23, 1919. Excellent progress in the tanning of fish leather is to be recorded, and a number of the difficulties obstructive to the development of the industry have been overcome by tanners in this field.

One company which is tanning fish skins has established a station in North Carolina and another in Florida for the capture of sharks and porpoises, and is meeting with success in its fishery for sharks. It is understood that the number of stations will be increased as rapidly as possible. Another company has recently acquired a site for a tannery in Washington which plans to tan the hides of sharks, beluga, hair seals, etc.

Samples of leather recently submitted show marked improvement in appearance over earlier samples. The leather is soft and pliable and appears to have ample strength for many uses. Arrangements have been perfected for the Bureau of Standards to make tests of the leather products as to durability, porosity, tensile strength, pliability, water absorption, wearing qualities, etc.

The nets which the bureau developed for the capture of sharks are proving successful and are being adopted for the fishery. At the fishery stations the liver oil is being extracted and the flesh converted into fertilizer, so that none of the material is wasted.

Tanning and Finishing Sheepskins. By F. T. Howard, *Lea. World,* Aug. 14, 1919. Of the raw materials, green, salted, and dry-salted skins give the least trouble, but the flint-dried skin needs very careful working through the preliminary operations. To get good results it is best to start correctly at the soaks, for this is one of the most important operations. If the skins have been heavily salted they should have more than one change of water, a running soak for preference; fresh skins need but a few hours to rid them of the blood and dirt. Dry skins need much more attention. To soften such skins borax gives no risk, but considerable assistance in soaking back to the natural condition without pricking the grain or injuring the fibers of the skin. Sodium bisulphite can also be used with good effect, only a small quantity being required, one pound to every 100 gallons of water in the soak. It prevents swelling, possesses antiseptic qualities, and has no injurious effect upon the wool.

Dry skins should be broken over the beam midway in the soaking process, and all skins should be put through the hydro-extractor or some squeezing appliance to remove the water before de-wooling takes place.

In using depilatory for painting skins the strength is usually determined by the class of goods to be pulled. The writer finds it a safe practice to dissolve sufficient sodium sulphide in cold water to register 14° Tw., slack lime separately, and add enough to the sodium sulphide solution to create a thin paste; paint each skin, folding it lengthwise, wool side out; then place in pile in cool atmosphere for pulling the next day. Before starting this the pelts should be washed from the pullers in clean water to remove the sulphide, when a little bicarbonate of soda may be added. The actual liming should be done in clean limes, giving the skins one haul up in liquor from the previous pack. After one or two days they should be put into new lime, the strength of which may be regulated by the amount of grease in the skins. Here is a very important point in the manufacture of sheepskin leather: the greasier the skins, the higher liming they should receive. A satisfactory basis is from 2 to 3 gallons of slaked lime per 100 pelts, hauling frequently for nine to twelve days. When they come from the lime they gain in firmness by being couched for a day or so before fleshing.

When fleshed the skins should be puered and drenched. Dog dung is still used extensively. The usually soft nature of river water will sometimes bring down pelts without the use of puer at all. One to two buckets of dung, strained through a sieve or tied up in a bag, thrown in the paddle, will suffice for several hundreds of skins. The great ruling factor is the judgment of the puerman himself; he adds water or excrement if the goods proceed too quickly or slowly until he secures the desired silky state. Temperature must, of course, be allowed for, and the thickness of the skins.

When low enough the goods are washed in warm water and scudded on the beam or machine. This should be well done and carefully, for it removes the surface filth and reduces the necessity for excessive pressure to remove the grease later. The real cleansing of the skins comes with the drenching. The puered goods are washed off in water, and placed in a vat or paddle of warm water containing two buckets of bran for each eight dozen skins, the temperature to be about 90° F. After the lapse of a few hours, fermentation becomes visibly active, and the skins are forced up to the top of the vat or paddle; they should then be well moved about and forced down again, and the drench vigorously stirred. The goods are allowed to remain 24 hours, then removed, slated, and washed in cold water.

For some forms of leather the puer is dispensed with and the drench only used. There are bacterial bates on the market which give first-class results, and are much more uniform in use than manure. In this case no drench need be used, but the grain may be cleared by a wash in solution of borax and warm water. Many firms pickle their skins before tanning, but the only advantage is that of holding back stock not required immediately.

The tanning is done in paddles, but the surplus grease must be removed first, and it is best done (when the skins have been running in old, weak liquor for a few hours) by the hydraulic press. They are taken from the tan, washed through warm water, and spread out smoothly between the plates, and the pressure applied gently at first, until the whole of the skins are set. The maximum pressure is then applied, consistent with the state of the goods—usually 2½ to 3 tons will suffice. When the grease has ceased to run, the plates are taken out, and the skins have the appearance of sheet iron. To get them into a soft condition again the pressed cakes are placed in a drum and given a good run in warm, soft water, which separates the skins. Some tanners add salt to the warm water, but it creates difficulties in the finishing for fancy colors, so that it is best left out. After running for half an hour in the drum they are in condition to return to the tanning paddles.

It is well to mention at this point that some variation of treatment is necessary in the tannage of skins for roller leathers as compared to basils. Assuming that the tanner does his own pulling, the skins are sorted directly after, and low limed in clean lime liquor, drenched fairly low, and well worked on the grain over the beam with a slate to remove all short hairs, etc. Nothing but perfect-grained skins are suitable for first-grade rollers, and the leather is required very tough, and generally as thin as possible, without losing its tensile strength in consequence. One means to obtain this reduction in substance is to take the skins, after machine shaving, and steep them in warm water, then drum in hyposulphite of soda, say, ½ pound to the dozen skins. As a light color is essential, only clean, light-colored liquors can be employed.

The preliminary tanning is done in weak bark or quebracho liquor for one day; then the goods are pressed and returned to the paddles for further tanning in liquors of increasing strength, blended from French chestnut extract, wattle bark, decolorized quebracho, or oak bark, commencing after pressing with 4° B. one day, 6° B. second, 8° B. third, and 10° B. the fourth.

The goods should now be sufficiently tanned to remove from the vat; they are then washed through water to remove excess of tan and taken to be dried out. The longer this stock lies in the crust the better, but, when taken to finish, the skins should be sorted into different substances, usually about three, and shaved very accurately. The skins are next given a drumming in warm sumac solution, rinsed in water, drained, and struck out, then tacked on boards to dry out. In tanning these skins weight and plumpness is not a factor; the object is to have a thin, firm, pliable piece of leather, with a light-colored grain.

When dry take the skins off the boards, trim the nail holes out, and perch by hand to soften them. Now color and season light yellow, using ½ ounce of a suitable dye to an ordinary bucket of water; boil the color in a small quantity of water until dissolved. Separately boil 2 ounces of good soap, and when cool add to this ½ ounce egg albumen and a little milk, and mix with the yellow color. This mixture is sponged on the

skins with speed to get a good level color, two applications being usually necessary. The skins are next dried and rolled, perched again, and re-seasoned. Glazing follows, and, if necessary, ironing. The finished skins are now marked with a frame on the flesh side, trimmed with shears, wiped over with wool pad, and put into sizes.

There are many different methods and variations of process for tanning skins for colored work. Quebracho, for processed skins, produces a soft and excellent leather. Hemlock-tanned skins likewise produce a good color, on which it is easy to apply aniline dyes. Hemlock-tanned skins are finished in the natural color of the tan, dyed or colored, and finished with a smooth or embossed grain. A good tanning process for these goods consists of starting the skins in weak combination liquor of solid or liquid quebracho and gambier in a paddle with an average of 20 dozen skins until the grain is well set, and then the skins may be pressed. From the press, many modifications can be applied, having in view the particular object for which the skins are destined, but for unprocessed goods quebracho is too soft and empty a tannage, except where direct soft goods are aimed at. A well-blended mixture of bark liquor, with quebracho or chestnut, wattle and quebracho, wattle and gambier, and so on, will gain firmness.

After tanning, the skins are washed, sammed, shaved, set out, and hung up to dry, piled away in the crust, until they are required for finishing purposes.

The use of sumac after the regular tanning process is complete is to prepare the leather for coloring. It is usually done in a drum, and, if soft leather is wanted, the skins can be run with a combination of sumac and a little sulphonated oil; but great care has to be exercised in the amount of oils and fat-liquors these goods receive when intended for fancy colors, and also when they receive it, too.

The first false step often made in dyeing leather is in the selection of the dyestuffs; cheap dyes are always a blunder, and no good results can be achieved when they are used. Again, when enough dye is not used, dull, hungry-looking shades result. Good colors can be obtained by using the following process of dyeing. The leather, washed and cleaned, is drummed in a solution of sumac, using 2 per cent. in sufficient water to drum for one-half hour. One-half per cent. of tartar emetic, dissolved in hot water, is added and the leather is drummed one-half hour longer. Wash the leather and prepare the color solution.

For acid aniline dyes 4 ounces of formic acid for each 100 pounds of leather should be added to the dye liquor, and the leather drummed until it is evenly colored. The dye liquor is added in portions of one-third, and drumming continued for another half-hour, at the end of which time the leather should be washed, and fat-liquored with 2 per cent. of sulphonated oil, struck out very carefully, and tacked on frames to dry.

Upon leather that is dried after tanning without fat-liquoring it is good practice to dye with titanium potassium oxalate and aniline dye; then wash and fat-liquor it with 2 per cent. sulphonated or Turkey red

oil, and dry for finishing. The dry leather is weighed, and for each 100 pounds, 8 ounces of titanium is used, dissolved in warm water. The leather is first softened in warm water, and then drummed in the solution for ten minutes, which produces a yellowish brown color on which any shade of tan can be easily obtained. The skins are drummed in sumac before being given this treatment. With acid anilines the color can be given after ten minutes without being washed.

Beautiful shades of tan and brown are obtained by first drumming the leather in phosphine solution, combined with a shading brown, until the dye-bath is exhausted. Add while the drum is in motion 8 ounces of titanium potassium oxalate in solution for every 100 pounds of leather; run another ten minutes, wash and fat-liquor leather, and set it out, then tack on to frames and dry out.

If basic dyes are to be used after the titanium solution, the liquor must be run off, the skins washed, and the dye liquor applied. No tartar emetic or bichromate of potash is used, and the colors produced are fast to light and full in shade.

A good black can be obtained by the use of logwood and titanium potassium oxalate, using 10 to 12 ounces of the latter. Take the dry skins, soften them in warm water, then drum them in a solution of half the titanium for fifteen minutes. Now pour into the drum slightly alkaline logwood liquor, add the remaining half of titanium, and drum ten minutes more, when the leather should be washed, fat-liquored, set out and tacked on frames to dry.

Suède finished leathers are taken, after they are dried, and are buffed on the flesh side, first on coarse emery, and then on fine emery; softness and a short, smooth nap are the essential qualities. Crushed levant grain is obtained by embossing the skins, then seasoning and glazing them, as the grain must be flattened out. Two or three glazings are necessary to get the right finish. The colors are generally blue, red, green, brown, etc. The best results are obtained by coloring on the table after embossing. Various methods are adopted in finishing tanned sheep to obtain the end in view, but in nearly all cases it is to imitate some more expensive leather.

The Artificial Tannins. H. BAMBERGER, *Chem. Ztg.* 43, 318; *J. Soc. Dyers and Col.* 35, 223 (1919). The progress made in the synthesis of tannin materials is reviewed by the author from the chemical standpoint. In 1875, H. Schiff, in a paper on synthetic sulphurized tannins, describes the correct method for the preparation of such substances from phenol sulphonic acid, together with an almost correct explanation of the structure of these compounds. He obtained a substance with the general properties of a natural tannin, by the action of phosphorus oxychloride on phenol sulphonic acid, to which the formula $(HO).C_6H_4.SO_2.O.C_6H_4.(SO_3H)$ was ascribed. It is doubtful whether Schiff's product was the pure didepside of phenol sulphonic acid; more probably it was a mixture with polydepsides. The pure di- and tridepsides of phenol sulphonic acid were

obtained by E. Fischer and Zincke. Carbomethoxyphenol sulphonic chloride was condensed with the sodium salt of phenol sulphonic acid forming

$$(I.)\ CH_3O.C(O).O.C_6H_4SO_2.O.C_6H_4.SO_3Na,$$

which yielded the pure didepside on saponification. The pure didepside precipitates gelatine, but does not convert hide into leather. The compound (I.) was converted into the sulphonic chloride, condensed with a further molecule of the sodium salt of phenol sulphonic acid, and the product saponified, forming the tridepside

$$HO.C_6H_4.SO_2.O.C_6H_4.SO_2.O.C_6H_4.SO_3Na$$

in a pure state. The tridepside behaves towards hide like a true tannin. Numerous patents were taken out by the Badische Anilin und Soda-Fabrik to cover Schiff's work; the artificial tannins described are probably mixtures of polydepsides of phenol and cresol sulphonic acids.

The idea contained in many patents that an amorphous character is essential for a tannin no longer holds good, as the pure tridepside of phenol sulphonic acid is crystalline, and other crystalline tannins are described in later patents.

A patent of the Deut. Kol. Gerb. und Farb. Ges. covers the condensation products of α and β-naphthol and their sulphonic acids. Such compounds are probably the naphthalene analogues of the depsides of phenol sulphonic acid. It would be interesting to know whether the linking together of two naphthalene nuclei is sufficient to impart the property of tanning, or whether at least three residues are necessary in this case also. This information could readily be obtained via carbomethoxynaphthol sulphonic chloride.

A second class of tannins was first prepared by Stiasny by the action of formaldehyde on phenol sulphonic acids or phenols and sulphuric acid, and developed by the Badische Anilin und Soda Fabrik. The sirupy product, "Neradol D" used in large quantities in Germany during the war, was prepared in this manner. The Deut. Kol. Gerg. u. Farb. Ges. studied the action of formaldehyde on salicylic acid, cresotinic acid, and naphthol sulphonic acids, and found that tannins were produced by the action of formaldehyde on naphthylamine and amidonaphthol sulphonic acids. Röhm and Haas in Darmstadt found that the condensation product, phenol methane sulphonic acid, prepared from phenol, formaldehyde, and neutral sulphite, was an exceptionally good tannin. This reaction was extended to the alkali soluble condensation products of phenol and formaldehyde.

The author prepared tannins by condensing dioxydiarylethanes with formaldehyde and neutral sulphite. This reaction may be extended to diphenyloldimethylmethane (from acetone and phenol) and dioxytriphenylmethane. The tannins of this class are methane sulphonic acids. The Badische Anilin und Soda Fabrik found that dioxydiarylethanes are converted into tannins by sulphonation, which supports the hypothesis that tannins prepared from formaldehyde and phenol sulphonic acids are dioxydiphenylmethane sulphonic acids.

The author, in developing his work on this subject, believed that tannins could also be obtained by the substitution of hydroxyl groups by salt forming arylsulphamino groups according to three fundamental methods:

(1) Preparation of methane sulphonic acids of arylsulphamino benzene derivatives, *e. g.*, reduction of technical nitrobenzyl sulphonic acid sodium salt followed by condensation with *p*-toluene sulphonic chloride forming

$$CH_3.C_6H_4.SO_2.NH.C_6H_4.CH_2.SO_3Na.$$

(2) The action of formaldehyde on arylsulphaminoaryl sulphonic acids, *e. g.*, the condensation product of *p*-toluene sulphonic chloride with aniline and naphthylamine sulphonic acids reacts with formaldehyde in neutral or acid solution, preferably at a high temperature and pressure, forming easily soluble tannins.

(3) Preparation of di- and polydepsides containing arylsulphamino groups instead of hydroxyl groups, *e. g.*, compounds such as

$$NaSO_3.C_6H_4.NH.SO_2.C_6H_3(CH_3).NH.SO_2.C_6H_4.CH_3$$

or

$$NaSO_3.C_6H_4.NH.SO_2.C_6H_3(CH_3)NH.SO_2.C_6H_3.$$
$$(CH_3)NH.SO_2.C_6H_4.CH_3,$$

containing two or more aryl sulphamino residues, are readily prepared from nitrotoluene sulphonic chlorides. These colorless crystalline compounds are of a tannin nature, and react with formaldehyde, forming amorphous substances.

Leather Dyeing. E. O. RASSER, *Bayer Ind. u. Gewerbeblatt.*, 105, 41, (1919); *J. Soc. Dyers and Col.* 35, 221 (1919). Advances in the production of shades fast to light and water in leather dyeing are described. For chrome leather, sulphide dyes are used, if necessary with an after-treatment of fat. Good results are obtained in leather dyeing by the direct use of mineral colors (Titanium, Wolfram, and Vanadium salts). Fat soluble dyes are especially suitable for certain classes of leather. Yellow is obtained by treatment with a solution of lead acetate followed by a solution of potassium bichromate. Red may be produced by treating the leather with water containing a little nitric acid, followed by an ammoniacal extract of finely powdered cochineal, or by successive treatments with solutions of potassium chromate and silver nitrate. Blue may be obtained by treatment with a dilute aqueous solution of indigo carmine, or by steeping in a ferric chloride solution followed by potassium ferrocyanide. Green is obtained by steeping in a solution of two parts verdigris and one part ammonium chlorite. Brown is obtained by dyeing with a potassium permanganate solution containing soda. Grey results by steeping in a very dilute lead acetate solution, followed by exposure to an atmosphere of sulphureted hydrogen. Black is produced by treating leather with a solution containing logwood extract and a tannin followed by ferrous sulphate solution. For chrome leather, substantive dyes which may be

coupled with diazonium compounds, *e. g.*, the Paranil colors, are used in combination with diazotized *p*-nitraniline. The chrome leather, free from acid, is treated with a solution of the Paranil color at 50° C., then with a solution of diazotized *p*-nitraniline at 20°, and finally with an emulsion, containing 2 per cent. soap and 0.5 per cent. neatsfoot oil. Chamois leather, after removal of fat, is treated with 2 per cent. chrome alum solution, then with a Paranil color, diazotized *p*-nitraniline, and finally with a soap emulsion.

Chrome Leather Waste. *J. I. E. C.* 11, 884. A German patent for the utilization of chrome leather waste has been introduced by A. Wolff, Hamburg. The waste is dissolved in sufficient sulphuric acid (about 5 per cent.) at 80-90° C., and, after the removal of the fat which separates, the chrome is precipitated as hydroxide together with calcium sulphate by the addition of an excess of lime and is then converted into chrome alum. The gelatin is recovered from the solution after precipitating the dissolved lime and calcium sulphate by treatment with carbonic acid and barium carbonate. For trimmings as obtained in chrome tanneries, the weight of 5 per cent. acid used is equal to that of the waste, while for waste from shoe factories the proportion of 5 per cent. acid is approximately three times as great.

Quantitative Separation of Glue and Similar Substances in Vegetable Glues. W. Donselt, *Z. Spiritusind.* 42, 44 (1919); *Chem. Zentr.*, 90, II., 590 (1919); *J. S. C. I.* 38, 547A (1919). Ten grams of material is intimately mixed with 250 cc. of warm water and boiled for 4-5 hours under a reflux condenser, 1-2 grams of tartaric acid is then added and the boiling continued for a further 30 minutes. The mixture is nearly neutralized with sodium hydroxide, the albuminous matter precipitated by the addition of a saturated solution of zinc or copper sulphate, and the solution made up to a definite volume and filtered. The nitrogen is then determined both in the residue and in the filtrate by Kjeldahl's method. To determine the amino nitrogen an aliquot part of the filtrate is precipitated with dilute tannin solution acidified with acetic acid and the nitrogen again determined in the filtrate. This latter value subtracted from the value obtained before precipitation with tannin gives the true nitrogen value of the glue content.

The Tanning Industry in South and British East Africa. By Charles Le Petit, *Le Cuir* 8, 215 (1919). Up to 1912, in spite of considerable local advantages, there was very little development of the industry in South Africa because of the blind preference of capital for agricultural and mining enterprises. But since the war began, important tanneries have been established at Natal, Lourenco Marques, and other places, which are now producing good leather at a price with which the imported products of Europe and America cannot compete locally. The most modern methods of rapid and mixed tannages are used. The chief tanning material, silver wattle bark, grows extensively in the region of Natal and gives a good yield of leather of excellent quality.

East Africa offers even greater opportunities for the future than South Africa, possessing plenty of hydraulic power, coal, skilled labor at low cost, and an abundance of raw materials such as the dried skins of buffaloes, goats, antelopes, and gazels, as well as large plantations of black wattle bark rich in tannin. British rule is praised as giving security to new enterprises. Although a tanning industry has already been established by British interests, Le Petit urges his countrymen that chrome tanning and the manufacture of mimosa and chestnut extracts still offer a vast field for French enterprise in this prosperous country.

J. A. W.

The Tanning School at Liege. By M. GILKENET, *Le Cuir* 8, 216 (1919). (Preliminary Note: The future of the Tanning School, because of the war, is still somewhat in doubt, and Mr. Kilkenet has been appealing for its re-establishment.) Twenty-one years ago a group of Belgian tanners decided to form an association for giving instruction in tanning under the auspices of the Liège Leather Stock-exchange. The beginning was slow and difficult, it being a question of introducing modern chemistry into a routine industry. But, little by little, thanks to the efforts of the eminent chemist, Professor Nihoul, the school acquired great renown and future tanners came from all parts of the world to be initiated into the secrets of leather chemistry. The course required two years, the second being devoted largely to laboratory practice in the analysis of materials used in the tannery. The instruction in leather manufacture was chiefly theoretical as most of the students were sons of tanners and already familiar with tannery practice. The school is situated in the center of the city of Liège and contains, besides lecture rooms, two magnificent laboratories and a library equipped with all important books and periodicals pertaining to the industry. A list of the publications of Professor Nihoul and two photographs of the laboratories are included.

J. A. W.

The Use of Chromic Sulphate for Chrome Tanning. By J. JETTMAR, *Gerber* 45, 233. Formerly potassium bichromate and chrome alum have been generally used for chrome tanning, only occasionally sodium bichromate, chromic chloride, chromic sulphate and some organic chromium compounds, especially chromium formate has also been employed. Lately large quantities of chromic sulphate have come on the market which will well cover the present scarcity of the more commonly used chrome salts. Its application is exactly similar to that with chrome alum.

Chrome alum is a double salt of potassium sulphate and chromic sulphate and contains 24 molecules (about 43.2 per cent.) water. Potassium sulphate exerts no tanning action, only the chromic sulphate, and alum contains approximately 39.9 per cent. giving 15.3 per cent. chromic oxide (Cr_2O_3).

Chromic sulphate in commerce comes usually in solution although the solid salt can be obtained. The latter when pure contains

38.93 per cent. chromic oxide and 61.07 per cent. sulphur trioxide, crystallized it contains 18 molecules (or 45.2 per cent.) water, whereby the chromic oxide content is lowered to 21.3 per cent.

In trade, liquid chromic sulphate comes mostly in strengths of 30, 35, 40 and 45° Bé. (containing approximately 26.0, 31.0, 34.2 and 39.7 per cent. $Cr_2(SO_4)_3$ or 9.4, 11.2, 12.8 and 14.4 per cent. Cr_2O_3 respectively. A one bath liquor is prepared with chromic sulphate as follows: The chrome liquor is diluted to give a solution containing 3.5 per cent. chromic oxide (11° Bé.). If one has a chrome liquor originally of 35° Bé., add to 10 liters of the chrome solution 22 liters of water and agitate thoroughly. At the same time dissolve 3 kilograms of soda crystals (or 1.1 kilograms anhydrous soda, or ammonium or solvay soda) in 5 liters of warm water and add this solution while stirring to the chromic sulphate solution. This effervesces strongly and should always be done in a large enough container. The addition of soda solution is continued until a permanent precipitate results. From this point it is well to add a little more soda and to redissolve the precipitate by the addition of formic acid. An addition of formalin (about ½ liter of 40 per cent. formaldehyde) expedites the tannage. Finally the liquor obtained is diluted with pure water to 37 liters and a chrome liquor is obtained containing almost exactly 3 per cent. chromic oxide. This stock solution can then be used in the usual manner.

Instead of soda the liquor can also be made basic with whiting as Eitner has recommended for chrome alum. The whiting is simply added to the chromic sulphate solution while stirring until a permanent precipitate is formed. The calcium sulphate formed settles to the bottom. The supernatant basic chromic liquor is removed and treated eventually with formic acid and formalin and diluted with water as directed above. However, with the use of soda or whiting a chrome solution of exactly the same basicity is only obtained by using exactly the same conditions each time and for this reason Eitner recommended the use of sodium thiosulphate in preparing chrome extracts. With the use of chromic sulphate a 10 per cent. chromic oxide solution (32° Bé.) is prepared. Thirty liters of this solution is boiled and to it is added slowly while stirring a solution of 5 kilograms of sodium thiosulphate dissolved in 15 liters of warm water. Sulphurous acid escapes and free sulphur is thrown down. The clear solution is removed, diluted to a known chromic oxide content and used as stock liquor. It is considered very appropriate to remark here that instead of potassium bichromate, sodium bichromate should be used. The former is made from the latter and must necessarily be more costly, with its use potash is lost which serves as a valuable fertilizer for farming while it is entirely worthless to tanners. Moreover sodium bichromate is very similar to the potassium salt. It has the disadvantage that it is hygroscopic and therefore deliquesces in the air, therefore, it must be stored in closed containers.

G. W. S.

Specifications for Leather Belting. By H. A. Hey, *Ind. Management,* April, 1919, *Paper,* May 7, 1919. The purchase of leather belting presents manifold difficulties to the purchaser in the way of reaching a decision as to the quality. No specifications have been adopted by any engineering society or association of manufacturers. A few individual buyers have adopted specifications but in many cases they conflict. Unlike most modern specification they do not specify what is desired and the tests to be met but are largely confined to describing how the belting should be made. Specifications for general use should state clearly and concisely what class of material is wanted, what it is to be used for, what the inspection requirements will be and how the tests will be performed; and to this end the author offers his experience. Accumulated experience in the transmission of power by belting has shown conclusively that the best material for general industrial use is leather, and that, on the basis of the lowest cost per year and greatest efficiency of service, first quality leather is superior. Hence the following data and comments apply only to first quality, oak-tanned leather belting.

Good belting should be strong, pliable, durable and free from any defects which will give trouble in service.

Strength is required sufficient to pull the load, with a large factor of safety to cover heavy emergency overloads, the severe strains due to throwing the belt on and off the pulleys, the weakening effects of rubbing against shifters, hangers and parts of machines, and accidental injuries of various kinds.

Pliability, the great importance of which is not recognized by most makers and users of belting, is essential to the economical transmission of power. A belt which does not hug the pulley will slip and consume power without doing useful work. Many belts are short-lived because of the burning which takes place from slippage when they are new.

Durability is the chief difference between a good leather belt and a cheap one. A really high grade belt, properly installed and protected from abuse will last an astonishingly long time.

Serviceability is especially important. Once a belt is put to work it should require as little attention as possible. It should run true, be free from excessive or uneven stretch and its joints should not come apart.

Some of these qualities are in direct conflict with each other and it is therefore important that none be over-developed at the expense of other essentials. Strength may be increased at the expense of pliability or by the use of the stronger but less compact belly stock at a sacrifice of durability and accompanied by excessive stretch. Pliability may be increased at the expense of long life and freedom from operating trouble. It is possible also to practically eliminate stretch on the pulleys by excessive stretching during manufacture, but a belt so treated has lost its resilience and its life will be short. The best belt is that in which the skill of the maker has operated to bring about the most satisfactory compromise between all the desirable qualities.

The strongest part of a hide is well down on the side, near the belly, but the fiber is not so firm and well knit as near the backbone. The quality area of a prime steer hide extends from 15 to 18 inches on either side of the backbone and from the root of the tail about 48 inches toward the shoulder. This area is known as center stock and will test well over 4,000 pounds per square inch tensile strength, with an elongation of 15 to 20 per cent.

The proper way to specify belt strength is in pounds per inch of width. Formulas for the transmission of power are invariably given in this unit for the reason that they are based on the friction between belt and pulley, which in turn is a function of belt width.

Tanning processes may either increase or decrease the thickness of the hide, yielding a great difference in strength per square inch, since the amount of fiber on which strength is dependent remains the same. It is also easily possible to give leather an artificial weight by introducing during the tanning and currying processes certain cheap loading materials which add nothing to the value of the belt but are paid for by the buyer at the high price of leather. If for no other reason than to discourage such practices, all reference to weight should be eliminated from specifications.

Other qualities being equal, the user would prefer a very thin belt which has certain inherent advantages. Makers should therefore be encouraged to develop a thin but strong and pliable belt. As belt makers buy leather by the pound and sell it by the foot, the emphasis would be placed where it should be, on quality, by specifying strength per inch of width.

All belting used for the transmission of power should be as pliable as possible. A stiff belt will not take a good grip on the pulleys at ordinary tensions. Many a belt is so badly burned by excessive slip when first applied as to lose much of its fiber strength. Such belts may appear to work well after a time but are short-lived. A good belt mounted on a properly designed drive should carry its load when running slack on the return side but this result is seldom attained in practice. Frequently this is because of the stiffness of the belt, which is overcome by excessive tightening. The increased bearing pressures resulting from this high tension greatly increase power consumption. The author's experiments and observations have established; 1, that a belt initially pliable will nearly always remain more pliable than a stiffer one; 2, that it is possible to set up a standard which may be expressed in definite units; and, 3, that the degree to which this requirement has been met may be determined by a simple test which may be performed at any time or place with concordant results.

This test consists in laying a piece of belt across a curved block. Small buckets are attached at each end by means of hooks and sand or shot is slowly poured into them until the belt bends sufficiently to touch the lower edges of the block. The total weight of both buckets and contents, divided by the width of the belt gives a measure of the pliability in ounces per inch of width.

This test is very delicate, revealing distinct differences between belts whose differing degrees of pliability can scarcely be distinguished by hand.

It must be remembered, however, that pliability may be secured at the expense of that firmness which makes for durability and smooth performance.

Of the whole area of a hide, less than half is suitable for first class belting from the standpoint of durability. This covers the back and upper sides of the animal, from the tail to the shoulder. In this area the fibers are firm and well-knit, the surface is less wrinkled and thickness and strength are more uniform. Lower side and belly stock is strong but stretchy. It is used for second-quality belting, which finds some excellent applications where conditions are destructive and long life cannot be expected. Shoulder stock is coarse-fibered, wrinkled and stretches unevenly, finding its market chiefly in leather specialties such as straps, washers, packings, shoe parts and in cheap one-season agricultural belting.

Center stock should therefore be specified for the best belting. If of good tannage and well made, such belting will prove far more durable than any other grade, amply justifying the difference in price. "Piping" will not take place in this area where it will in the inferior portions.

One of the most important processes in belt making is currying. This consists in stuffing the hide with greases which lubricate the dry fibers and permits them to rub against each other without breaking down. Best practice calls for the use of a mixture of edible beef tallow and cod liver oil, but it has never been proven conclusively that other greases may not be employed with equally good effect. A belt in service gradually loses a portion of this lubricating material and unless it is renewed at the proper time the life of the belt will be shortened.

Improper drying, poor tannage or too low a grease content will cause belts to crack when bent sharply with the grain side out. This should never be found in good belting.

For the purpose of identifying the origin of an unsatisfactory belt, the maker's name and brand should be stamped firmly into the leather every 10 feet. The same machine which does this may also be employed to mark the length every foot for convenience in cutting. The date of manufacture should also be stamped into the belt as a check upon durability. In order to make this check reliable, care must be exercised not to hold belts in stock too long.

A belt is obviously no stronger than its weakest joint and since joints occur about every 4 feet of length, as well as between the plies of double and triple belts, every care should be taken to make them as strong as possible. With good glue, properly mixed and applied with competent workmanship to a well prepared lap, a belt should never come apart at the joints. A joint strength of 90 to 100 per cent. of the leather strength should be maintained.

Of considerable importance on many drives, especially at high speeds, is uniformity of thickness. Lumpy belts are the cause of vibrations in the driven machinery which may result in rapid wear on bearings, damage

to delicate tools and chatter marks on the work. By proper selection of the stock and if necessary a reasonable amount of leveling, a variation within $^1/_{32}$ inch can be maintained.

Less serious, but worthy of attention, is variation in width. Belts too wide sometimes cause trouble on flanged pulleys or rub against projecting surfaces. An allowance of $^1/_{32}$ inch either way from nominal size should be sufficient.

One of the commonest faults in leather belting even among the best grades, is a high gloss finish resembling that usually seen on suitcases and similar leather goods. This slippery surface gives a low coefficient of friction on the pulleys and if the load is anywhere near normal for the belt, excessive slippage occurs until the surface is worn away and the leather underneath takes hold of the pulley. Such a belt is usually burnt in the process and has received a good start towards the scrap pile.

Manufacturers admit that such a finish is not best but insist that the average buyer, especially those who buy in small quantities through a dealer, are greatly influenced by appearance. For the same reason manufacturers refrain from sending out their product oil dressed unless so requested. This dressing, although of great value to the belt, darkens it and destroys the beautiful russet color of the natural steer hide. Hence for the sake of color, which is of no value, belts are deprived of the final touch which would add considerably to their pliability and keep them in prime condition for a much longer period.

Until buyers learn that color and polish are obtained at the sacrifice of much more desirable qualities and manufacturers have the moral courage to turn out the best possible product regardless of appearance, belting will be numbered among the list of commodities such as bleached flour and polished rice which are deliberately degraded to satisfy a foolish public whim.

Shimming is the insertion of thin strips of leather between the plies of a double or triple belt to bring it up to uniform thickness. This is open to the objection that it introduces additional cemented joints, any one of which may come apart. Proper selection of strips and overlapping of joints should make shimming unnecessary.

The following specification, based upon the principles outlined above, has been in satisfactory operation for the purchase of a large amount of belting during the past three years. It has not resulted in raising the price to the consumer over that customarily paid for first quality belting. The manufacturer has not been obliged to change his usual methods but has had to be vigilant in maintaining them at a high standard. The inspection has not been found burdensome or expensive.

SPECIFICATIONS FOR FIRST QUALITY OAK-TANNED LEATHER BELTING.

1. These specifications are intended to cover first quality, center-stock, oak-tanned leather belting for general use. Previous specifications are hereby cancelled.

2. The material and workmanship must be guaranteed by the vendor to be of the highest quality and the finished product equal in strength,

pliability, durability and performance in use to any obtainable in the market.

3. The purchaser reserves the right to subject each roll of belting when received to the following tests. Failure to pass any of them will be cause for the return of the entire roll for full credit, plus carrying charges both ways. The manufacturer's name and brand must be stamped on all belts every 10 feet and the length every foot.

4. When unrolled freely on a flat surface, without tension, the belt must lie flat at all points and be full length as marked. There must be no evidence of injurious surface blemishes, artificial finish to produce high polish, shimming or excessive leveling, cracking when bent grain side out through 180° over a ½ inch diameter rod for single belts and a 1 inch rod for double belts or piping when similarly treated grain side in.

5. No section shall be longer than 54 inches or shorter than 42 inches, including laps, except in double belting, where shorter pieces may be used provided they do not exceed 10 per cent. of the total number of laps.

6. (*a*) Thickness must not vary more than 1/32 inch; (*b*) width must be within 1/32 inch of nominal size.

7. Character of leather must be uniform throughout the entire length of the belt.

8. One or more test pieces 1 inch wide will be cut at random lengthwise of the belt. Each test piece must show a tensile strength in pounds per inch of width not less than the following table. The vendor may furnish any thickness or weight of belting which will meet this requirement. Total elongation at the required load must not be less than 15 per cent. nor more than 20 per cent. in 2 inches:

	Single			Double		
	Under 2 inches	2 to 4 inches	Over 4 inches	Under 4 inches	4 to 8 inches	Over 8 inches
Light	580	605	630	900	1000	1100
Medium	630	675	720	1100	1200	1300
Heavy	720	765	810	1300	1400	1500
Extra heavy	810	900	990	....	...	....

9. Cemented joints must not crack or yield before reaching a load equivalent to 90 per cent. of the tensile strength specified in paragraph 8.

10. A section 40 inches long and the full width of the belt will be tested for pliability by being suspended over a form of the dimensions shown, grain side down, and weighted at each end. Both ends must touch the bottom corners at a total weight per inch of width within the following limits:

	Minimum ounces	Maximum ounces
Light, single	8	15
Heavy, single	10	20
Light, double	45	60
Heavy, double	60	80

11. The total lubricating matter shall be increased by oil dressing to approximately 12 to 15 per cent. by weight when examined in accordance with the practice of The American Leather Chemists' Association. Chemical examination shall not show loading for artificial weight, free mineral acid or anything detrimental to the strength, pliability or durability of the belt.

12. Belting must not run unevenly on the pulleys, show excessive stretch or develop other defects of material or workmanship in service, when properly applied.

G. W. S.

PATENTS.

Tanning, Etc. British Patent 128,339. R. KAY and G. A. PLATT, Warrington, May 8, 1918. Apparatus for tanning, liming, and like operations on hides and skins comprises a series of pits connected together by pipes so that the overflow from the top of a pit passes down to the bottom of the next pit, and a leaching-vat, etc., which supplies liquor by a pump to the bottom of the first pit and takes liquor up from the top of the last pit.

Leather Making. British Patent 128,484. R. W. JAMES, London, Oct. 11, 1918. A machine for dehairing hides, etc.

Vats. British Patent 128,451. C. M. OWENS, Warrington, Lancashire, July 31, 1918. The liquor in tanning vats is agitated by a number of paddles mounted on shafts and having an up-and-down vibratory movement, the paddles being located near the bottom of the vat.

Lactic Acid. British Patent 128,687. A. P. H. DESBOROUGH, J. REILLY and A. C. THAYSEN, all in Dorsetshire. April 20, 1918. Lactic acid is formed by fermenting sugars, such as maltose, which may be obtained by the action of malt or moulds upon cereals, chestnuts, acorns, etc., dextrose, saccharose, mannite, raffinose, and arabinose, with a new type of lactic-acid producing organism, *viz., bacterium volutans,* which is found in sour mashes, maize or other cereal meal, soil, carrots, and parsnips and is identified by the size and by the production of volutine which can be detected microscopically by staining with polychrome methylene blue solution. The acidity developed by the fermentation is reduced by repeated addition of preferably sterilized alkali, alkaline-earth compounds such as calcium carbonate or oxide, or other oxides, hydroxides, or carbonates such as zinc or ammonium compounds. The lactates may be separated by evaporation and crystallization, and other lactates obtained by double decomposition. The crude lactates may be washed with small quantities of water, and the wash-liquors worked up for separation of volatile fatty acids, such as acetic or butyric, which are formed during the fermentation. The lactates may be decomposed with sulphuric or other

acid, and the lactic acid separated by extraction with butyl or isobutyl alcohol. Volatile fatty acids may be separated from the lactic acid by distillation. The lactic acid may be purified by converting it into lactide by heating in a current of air or otherwise, separating the lactide by distillation under reduced pressure, purifying it by crystallization, and reconverting it into lactic acid by heating with lactic acid solution, or into lactates by treatment with metal hydroxides. Solutions for fermentation may be obtained by treating brewers', distillers', or other mashes which have been spoiled by entry of foreign organisms by saccharifying with malt if necessary, and boiling.

Dyes from Natural Products. British Patent 129,761. R. H. and M. H. VEGAS, Buenos Aires, Argentina, June 14, 1918. A coloring matter, useful for coloring food products, etc., and also as a mordant in dyeing textile materials, etc., is extracted from the bark, wood, roots, or leaves of the Retama tree found in the Argentine.

Tanning. British Patent 128,835. G. RANDALL, Worcester, Nov. 21, 1918. A frame for carrying and suspending hides in a liming or tanning pit.

Tanning. British Patent 130,010. R. SILBERBERGER, Klattau, Bohemia, Nov. 17, 1917. In obtaining tanning extract from pine-tree bark, the resin is removed before lixiviation of the bark. The solvent employed for the resin must have a boiling-point of slightly over 100° C. at atmospheric pressure, so that drying of the water in the bark can be carried on simultaneously with the extraction of the resin, thus avoiding loss of the tanning material in the resin solvent. Subsequent lixiviation of the bark with warm water produces a concentrated tanning liquor.

Leather-Finishing Process. U. S. Patent 1,311,188. ROLAND L. SMITH, Everett, Mass., May 2, 1917. The process of resurfacing damaged enamel which consists in applying to the damaged portion a suitable filler, frictionally treating the filler and adjacent enamel with a solid oleaginous composition having a granular caustic material intimately mixed therein, etc.

Journal of the

American Leather Chemists Association

Vol. XIV DECEMBER, 1919 No. 12

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Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $6.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized July 16, 1918.

FIRST MEETING OF THE SOCIETY OF LEATHER TRADES' CHEMISTS.

The first meeting of the S. L. T. C. was held in the Chemical Theatre of the Sorbonne, Paris, on September 22 and 23, 1919, Professor L. Meunier presiding.

Dr. J. G. Parker, chairman of the Sole Leather Analysis Committee, reported on the results that had been obtained by this committee, which was reappointed to continue its work.

C. F. Barber reported the results obtained by the Committee on the Analysis of Sulphonated Oils.

Among other things the official hide powder method for tannin analysis received considerable discussion.

The officers elected for the next two years were as follows:—

President—Dr. J. Gordon Parker.
Vice-President—Prof. L. Meunier.
Prof. Ed. Nihoul.
Hon. Treasurer—A. Seymour-Jones.
Hon. Editor—Prof. H. R. Procter.
Hon. General Secretary—Dr. A. Gansser.
Editorial Committee—Two representatives from each Section to be nominated to act as translators and abstractors.

METHODS OF THE A. L. C. A. 1919.

Official Method for the Analysis of Vegetable Materials Containing Tannin.

1. Raw and Spent Materials.

(1) *Caution:* Proper care must be taken to prevent any change in the water content of raw materials during the sampling and preliminary operations. (See "General" under Sampling.)

(2) *Preparation of Sample:* The sample must be ground to such a degree of fineness that the entire sample will pass through a sieve of 20 meshes to the inch (linear).

(a) The temperature used for drying samples of spent material for grinding must not exceed 60° C.

(b) Samples of raw material too wet to be ground may be dried before grinding as in (a). In this case a preliminary water determination must be made according to (IV) on the sample as received. If the portion of the sample taken for the water determination is in pieces too large to dry properly, it is permissible to reduce these to smaller size as rapidly and with as little loss of water as possible.

(3) *Water Determination:* Ten grams of the ground material shall be dried in the manner and for the period specified for evaporation and drying in extract analysis (see IV).

(4) *Amount of Sample to Be Extracted:* Such an amount of raw material shall be extracted as will give a solution containing

as nearly as practicable 0.4 gram tannin to 100 cc. (not less than 0.375 or more than 0.425). Of spent materials such an amount shall be taken as will give a solution of as nearly as practicable the above concentration.

(5) *Extraction:* Extraction shall be conducted in an apparatus consisting of a vessel in which water may be boiled and a container for the material to be extracted. The container shall be provided above with a condensation chamber so arranged that the water formed from the condensed steam will drip on the material to be extracted, and provided below with an arrangement of outlets such that the percolate may either be removed from the apparatus or be delivered to the boiling vessel. The boiling vessel must be so connected that it will deliver steam to the condensation chamber and that it may receive the percolate from the container. The condensation water from the condenser must be at approximately the boiling temperature when it comes in contact with the material to be extracted.

The material of which the boiling flask is composed must be inert to the extractive solution. Suitable provision must be made for preventing any of the solid particles of the material from passing into the percolate.

(A) Woods, Barks and Spent Materials:

Five hundred cc. of the percolate shall be collected outside in approximately 2 hours and the extraction continued with 500 cc. for 14 hours longer by the process of continuous extraction with reflux condenser. The applied heat shall be such as to give condensation approximately 500 cc. in 1½ hours.

(B) Materials Other than Woods, Bark and Spent:

Digest the material in the extractor for 1 hour with water at room temperature and then extract by collecting 2 liters of percolate outside in approximately 7 hours.

(6) *Analysis:* The percolate shall be heated at 80° C., be cooled, made to the mark and analyzed according to the offiical method of extracts.

II. Analysis of Extract.

(7) *Amount and Dilution for Analysis:* (A) Fluid Extracts: Fluid extracts shall be allowed to come to room temperature, be

thoroughly mixed, and such quantity weighed for analysis as will give a solution containing as nearly as possible 0.4 gram tannin to 100 cc. (not less than 0.375 nor more than 0.425). Precautions must be taken to prevent loss of moisture during weighing. Dissolve the extract by washing it into a liter flask with 900 cc. of distilled water at 85° C.

Cooling:

(a) The solutions prepared as above shall be cooled rapidly to 20° C. with water at a temperature of not less than 19° C., be made to the mark with water at 20° C. and the analysis proceeded with at once, or

(b) The solution shall be allowed to stand over night, the temperature of the solution not being permitted to go below 20° C., be brought to 20° C. with water at not less than 19° C., be made to the mark with water at 20° C. and the analysis proceeded with.

(B) Solid and Powdered Extracts:

Such an amount of solid or powdered extract as will give a solution of the strength called for under liquid extracts shall be weighed in a beaker with proper precautions to prevent change of moisture. One hundred cc. of distilled water at 85° C. shall be added to the extract and the mixture placed on the water-bath, heated and stirred until a homogeneous solution is obtained. When dissolved, the solution shall immediately be washed into a liter flask with 800 cc. of distilled water at 85° C., be cooled, etc., as under (A) above.

NOTE: It is permissible to make up 2-liter instead of 1-liter solutions dissolving by washing into flask with 1,800 cc. water at 85° C. in case of fluid extracts and 1,700 cc. water at 85° C. in case of solid or powdered extracts.

(8) *Total Solids:* Thoroughly mix the solutions; pipette 100 cc. into tared dish, evaporate and dry as directed under "Evaporation and Drying." (See IV.)

(9) *Water:* The water content is shown by the difference between 100 per cent. and the total solids.

(10) *Soluble Solids:* S. & S. No. 590, or Munktell's No. 1F, 15 cm. single, pleated, filter paper shall be used for the filtration.

The kaolin used shall answer the following test: 2 grams kaolin digested with 200 cc. of distilled water at 20° C. for 1 hour shall not give more than 1 mg. of soluble solids per 100 cc., and shall be neutral to phenolphthalein. To 1 gram kaolin in a beaker add sufficient solution to fill the paper, stir and pour on paper. Return filtrate to paper when approximately 25 cc. has collected, repeating operation for 1 hour, being careful to transfer all kaolin to the paper. At the end of the hour remove solution from filter paper, disturbing the kaolin as little as possible. Bring so much as needed of the original solution to exactly 20° C. as described under (7), refill the paper with this solution and begin to collect the filtrate for evaporating and drying so soon as it comes CLEAR. The paper must be kept full and the temperature of the solution on the filter must not fall below 20° C. nor rise above 25° C. during this part of the filtration. The temperature of the solution used for refilling the paper must be kept uniformly at 20° C. and the funnels and receiving vessels must be kept covered.

Pipette 100 cc. of clear filtrate into tared dish; evaporate and dry as under (8).

(11) *Insolubles:* The insoluble content is shown by the difference between the total solids and the soluble solids, and represents the matters insoluble in a solution of the concentration used under the temperature conditions prescribed.

(12) *Non-Tannins:* The hide powder used for the non-tannin determination shall be of wooly texture well delimed and shall require between 12 and 13 cc. of N/10 NaOH to neutralize 10 grams of the absolutely dry powder.

(a) Digest the hide powder with 10 times its weight of distilled water till thoroughly soaked. Add 3 per cent. of chrome alum, $(Cr_2SO_4)_3K_2SO_4 24H_2O$, in 3 per cent. solution calculated on the weight of the air-dry powder. Agitate frequently for several hours and let stand over night. Squeeze and wash by digesting with 4 successive portions of distilled water, each portion equal in amount to 15 times the weight of the air-dry powder taken. Each digestion shall last for 15 minutes, and the hide powder shall be squeezed to approximately 75 per cent. water after each digestion except the last, a press being used if necessary. The wet hide powder used for the analysis shall contain

as nearly as possible 73 per cent. of water, not less than 71 per cent. nor more than 74 per cent. Determine the moisture in the wet hide powder by drying approximately 20 grams. (See IV.) To such quantity of the wet hide as represents as closely as practicable 12½ grams (not less than 12.2 nor more than 12.8) of absolutely dry hide add 200 cc. of the original analysis solution and shake immediately for 10 minutes in some form of mechanical shaker. Squeeze immediately through linen, add 2 grams of kaolin (answering test described under (9)) to the detannized solution and filter through single folded filter (No. 1F Swedish recommended) of size sufficient to hold the entire filtrate, returning until clear. Pipette 100 cc. of filtrate into tared dish, evaporate and dry as in (8).

The weight of the non-tannin residue must be corrected for the dilution caused by the water contained in the wet hide powder.

Funnels and receiving vessels must be kept covered during filtration. Flasks graduated to deliver 200 cc. are recommended for measuring the analysis solution to be detannized.

(b) Digest the hide powder with the amount of water and add the amount of chrome alum in solution directed under (a).

Agitate in some form of mechanical shaker for 1 hour and proceed immediately with washing and subsequent operations as directed under (a).

NOTE: In order to limit the amount of dried hide powder used, determine the moisture in the air-dry powder and calculate the quantity equal to 12½ grams of actual dry hide powder. Take any multiple of this quantity according to the number of analysis to be made, and after chroming and washing as directed, squeeze to a weight representing as nearly as possible 73 per cent. of water Weigh the whole amount and divide by the multiple of the 12½ grams of actual dry hide powder taken to obtain the weight of wet hide powder for 200 cc. of solution.

(13) *Tannin:* The tannin content is shown by the difference between the soluble solids and the corrected non-tannins, and represents the matters absorbable by hide under the conditions of the prescribed methods.

III. Analysis of Liquor.

(14) *Dilution:* Liquors shall be diluted for analysis with water at room temperature so as to give as nearly as possible 0.7

gram solids per 100 cc. of solution. Should a liquor be of such character as not to give a proper solution with water of room temperature it is permissible to dilute with water at 80° C. and cool rapidly as described under (7, A, a).

(15) *Total Solids:* To be determined as in Extract Analysis.

(16) *Soluble Solids:* To be determined as in Extract Analysis.

(17) *Insolubles:* Determined as in Extract Analysis.

(18) *Non-Tannins:* To be determined by shaking 200 cc. of solution with an amount of wet chromed hide power, containing as nearly as possible 73 per cent. water, corresponding to an amount of dry hide powder shown in the following table:

Tannin range per 100 cc.	Dry powder per 200 cc.
0.35——0.45 gram	9.0——11.0 grams
0.25——0.35 gram	6.5—— 9.0 grams
0.15——0.25 gram	4.0—— 6.5 grams
0.00——0.15 gram	0.0—— 4.0 grams

Solutions to be shaken for non-tannins as in Extract Analysis and 100 cc. evaporated as in Extract Analysis.

IV. Temperature, Evaporation and Drying, Dishes.

(19) *Temperature:* The temperature of the several portions of each solution pipetted for evaporating and drying, that is, the total solids, soluble solids and non-tannins must be identical at the time of pipetting.

(20) *Evaporation:* All evaporations and dryings shall be conducted in the form of apparatus known as the "Combined Evaporator and Dryer" at a temperature not less than 98° C. The time for evaporation and drying shall be 16 hours.

(21) *Dishes:* The dishes used for evaporation and drying of all residues shall be flat-bottomed glass dishes of not less than 2¾ inches diameter nor more than 3 inches in diameter.

V. Determination of Total Acidity of Liquors.

(22) *Reagents:* (a) One per cent. solution of gelatine neutral to hematine. The addition of 25 cc. of 95 per cent. alcohol per liter is recommended to prevent frothing. If the gelatine solution is alkaline, neutralize with tenth normal acetic acid and if acid neutralize with tenth normal sodium hydroxide.

(b) Hematine. A solution made by digesting hematine in cold neutral 95 per cent. alcohol in the proportion of ½ gram of the former to 100 cc. of the latter.

(c) Acid washed kaolin free from soluble matters.

(d) Tenth normal sodium hydroxide.

Directions: To 25 cc. of liquor in a cylinder that can be stoppered, add 50 cc. of gelatine solution, dilute with water to 250 cc., add 15 grams of kaolin and shake vigorously. Allow to settle for at least 15 minutes, remove 30 cc. of the supernatant solution, dilute with 50 cc. of water and titrate with tenth normal soda using hematine solution as the indicator. Each cc. tenth normal soda is equivalent to 0.2 per cent. acid as acetic.

VI. GENERAL.

(23) When materials containing sulphite-cellulose extract are analyzed, the fact that the material contains sulphite-cellulose extract shall be noted on the report.

(24) The test for the presence of sulphite-cellulose in a liquor or extract shall be as follows: Five cc. of a solution of analytical strength shall be placed in a test tube, 0.5 cc. of aniline added and the whole well shaken; then 2 cc. of strong hydrochloric acid added and the mixture again shaken. If at least as much precipitate remains[1] as is obtained when a comparison solution prepared as below is similarly treated, the material shall be held to contain sulphite-cellulose.

The comparison solution shall consist of sulphite-cellulose in the proportion of one part total solids to 2,000 cc. of solution, and as much tanning material, similar to that being tested, but known to be free from sulphite-cellulose, as will make up the solution to analytical strength.

(25) On public analytical work by members of this Association the fact that the Official Method has been used, shall be so stated.

Official Method for Sampling Tanning Materials.

General: Extract whether liquid or solid, and tanning materials in general all contain moisture. The amount of moisture varies with climatic conditions, but especially in liquid and in most solid extracts becomes less as the extract is exposed to the

[1] Neradol D gives the same reaction.

air. As the value of any material shown by analysis is directly dependent upon the amount of moisture contained, and as an exposure of a comparatively few moments may alter appreciably the amount of moisture it is apparent that the sampling in all its details should be done as quickly as consistent with thoroughness and with great care to expose the material as little as possible to the air. The portions taken as samples should be placed at once in containers as nearly air tight as possible, and preferably of glass. Wood, cardboard, poorly glazed crockery, etc., are all porous and more or less absorbent and not suitable for retaining samples.

Liquid extract cannot be accurately sampled when it contains any frozen material. A sample of extract taken after live steam has been run into the extract has not the same concentration as the original extract. A sample of spent bark which has been standing where dust from fresh ground bark has sifted into it does not represent the degree of extraction of the spent bark. Samples of liquor which have been kept with no preservative in them for some time do not represent the condition of the liquor when sampled.

All extracts and crude tanning materials shall be sampled as nearly as possible at time of weighing, and for every 50,000 pounds, or less, sampled a sample shall be drawn.

(1) *Solid, Powdered and Pasty Extracts:* The number of packages to be sampled out of a given lot shall be ascertained by taking a percentage of the total number of packages in the lot obtained in the following manner:—Divide the total number of packages by 100, multiply by 0.02 and subtract from 4.

Thus

$$4{,}700 \div 100 = 47$$
$$47 \times 0.02 = 0.94$$
$$4 - 0.94 = 3.06 \text{ per cent.}$$
$$4{,}700 \times 0.0306 = 144 \text{ packages.}$$

Provided that for lots of 200 packages and under 5 per cent. of the number of packages shall be sampled, and for lots of 10,000 packages and over 2 per cent. of the number of packages shall be sampled.

Whenever possible every Nth package shall be set aside for sampling while the extract is being removed. When this is not

possible, the packages shall be selected from as uniformly distributed parts of the bulk as possible.

Samples of as nearly equal size as practicable shall be taken from each package and these samples shall represent as nearly as may be, proportionally the outer and inner portions of the extract. These sub-samples shall be placed in a clean, dry closed container. When sampling is completed, the whole composite sample shall be broken up until it will pass through a sieve of 1-inch mesh; it shall be reduced to the required bulk by successive mixings and quarterings. From this bulk duplicate samples of at least 6 ounces shall be drawn from opposite quarters by means of a small flat scoop (and not by selecting a handful here and there). The sample shall be enclosed in the smallest clean, dry, glass receptacle, sealed and properly labeled.

NOTE:—Whenever possible the sample should be wrapped in paraffine paper and placed in the smallest straight-side glass receptacle; especially is this desirable during the warmer months of the year.

Sampling at place of manufacture shall be conducted by running a portion from the middle of each strike into a mold holding at least 2 pounds. These sub-samples shall be preserved with proper precautions against evaporation, and be sampled for analysis as above.

(2) *Liquid Extracts in Barrels:* The number of barrels of extracts to be sampled out of any given lot shall be not less than 10 per cent. of the whole number of barrels for every 50,000 pounds or fraction thereof. The barrels to be sampled shall be rolled and shaken from end to end until the contents are homogeneous. Whenever this is not possible the heads of the barrels shall be removed and the contents stirred until homogeneous, a sample of equal size to be taken from each barrel. These sub-samples shall be put together in a suitable closed container and be thoroughly mixed. From this bulk duplicate samples of at least 4 ounces shall be drawn and preserved in clean, dry, glass containers; sealed and labeled with such distinguishing marks as may be necessary.

(3) *Liquid Extract in Bulk:* The extract shall be agitated with air, be plunged or be mixed by some other efficient means until homogeneous. Equal samples shall then be taken from

different parts of the bulk, be placed in a proper container, be thoroughly mixed and sampled as described in (2).

(4) *Liquid Extract in Tank Cars:* The following methods are permissible:

(a) The extract shall be unloaded into clean, dry containers and sampled according to (3); or,

(b) The extract shall be mixed until homogeneous, by plunging through the dome or other effective means, then numerous equal samples shall be taken from as widely scattered parts of the bulk as possible. These samples shall then be placed in a suitable container, be mixed and sampled as in (2).

NOTE:—As it is almost impossible to secure a homogeneous mixture of the extract in a tank car, this method should be used only when no other is possible. Or,

(c) The extract shall be sampled as follows while the car is being unloaded.—A quart sample shall be taken from the discharge three minutes after the extract has begun to run; another quart sample shall be taken three minutes before the extract has all run out, and three other quart samples shall be taken at equal intervals between these two. These five samples shall be transferred to a suitable container as soon as taken, be thoroughly mixed and sampled as in (2).

(5) *Crude Tanning Materials:* A. Shipments in bags, mats or other similar packages.

A number of packages shall be sampled representing 2 per cent. of the weight for every shipment of 50,000 pounds or fraction thereof, by taking representative portions from each package. These sub-samples shall be mixed together and the bulk be reduced by mixing and quartering to the desired size. Duplicate samples of not less than 5 pounds each shall be preserved in air-tight containers properly labeled.

B. Shipments in bulk, bark, wood, etc., in sticks.

Sticks shall be taken from at least ten uniformly distributed parts of the bulk, be sawed completely through and the sawdust thoroughly mixed and sampled as in "A."

C. Materials prepared for leaching.

Samples of equal size shall be taken at uniform intervals as the material enters the leach and be kept in a suitable container till sampling is completed. This bulk shall then be thoroughly

mixed, be reduced by mixing and quartering, and duplicate samples for analysis of at least 2 pounds in size be preserved in air-tight containers, as in "A."

(6) *Spent Materials From Leaches:* Samples of spent material shall be taken from the top, middle and bottom, and in each case from the center and outer portions of the leach. These sub-samples shall be thoroughly mixed, be reduced in bulk by mixing and quartering, and duplicate samples of at least 1 quart in size be preserved for analysis.

(7) *Tanning Liquors:* The liquor shall be mixed by plunging or other effective means till homogeneous and then samples of at least 1 pint be taken for analysis. The addition of 0.03 per cent. of thymol or other suitable anti-ferment to the sample is essential to keep the liquor from altering its original condition.

When routine samples are taken from day to day and a composite sample analyzed, samples of equal size shall be taken from each vat after thorough mixing, be preserved in covered containers in as cool a place as possible, and be kept from fermentation by the addition of suitable anti-ferment, as above. This bulk shall be mixed till homogeneous and samples of not less than 1 pint each be preserved for analysis.

When a sample is taken by a member of this Association in accordance with the above method, it is requested that he state upon the label of the sample submitted and upon the analysis blank that "this sample has been taken in accordance with the official method of sampling of The American Leather Chemists Association."

Official Method for Analysis of Vegetable Tanned Leather.

(1) *Preparation of Sample:* The sample of leather for analysis shall be reduced to as fine a state of division as practicable, either by cutting or grinding.

(2) *Moisture:* Dry 10 grams of leather for 16 hours at a temperature between 95°-100° C.

(3) *Fats:* Extract 5 to 10 grams of air-dry leather in a Soxhlet apparatus until free from grease, using petroleum ether boiling below 80° C. Evaporate off the ether and dry to approximately constant weight.

Or, if preferred, extract 30 grams of leather as described above. In the latter case, the extracted leather, when freed of

solvent may be used for the determination of water-soluble material.

(4) *Ash:* Incinerate 10 to 15 grams of leather in a tared dish at a dull red heat until carbon is consumed. If it is difficult to burn off all the carbon, treat the ash with hot water, filter through an ashless filter, ignite filter and residue. Add the filtrate, evaporate to dryness and ignite.

(5) *Water-Soluble Material:* Digest 30 grams of leather in a percolator over night, then extract with water at 50° C. for 3 hours. The total volume of solution to be 2 liters. Determine total solids and non-tannins according to the Official Method for extract analysis.

(6) *Glucose:*

SOLUTIONS.

Copper Sulphate.—Dissolve 34.639 grams of $CuSO_4.5H_2O$ in distilled water and dilute to 500 cc. Filter through asbestos.

Alkaline Tartrate Solution.—Dissolve 173 grams of Rochelle salt and 50 grams NaOH in water and dilute to 500 cc. Allow to stand 2 days and filter through asbestos.

Normal Lead Acetate Solution.—Prepare a saturated solution of normal lead acetate.

DETERMINATION.

Place 200 cc. of leather extract of analytical strength in a ½-liter flask, add 25 cc. of a saturated solution of normal lead acetate, shake frequently (5-10 minutes), and filter. (The funnels and beakers must be kept covered to prevent evaporation.) Add to the filtrate an excess of solid potassium oxalate. Mix frequently for 15 minutes and filter, returning the filtrate until clear. Pipette 150 cc. of this filtrate into a 600 cc. Erlenmeyer flask, add 5 cc. of concentrated HCl and boil under a reflux condenser for 2 hours. Cool, neutralize (place a small piece of litmus paper in the flask) with anhydrous sodium carbonate, transfer to a 200 cc. graduated flask and make to volume. Filter through a double filter. (The filtrate must be clear.) Determine the dextrose in the solution immediately.

Place 25 cc. of the copper solution and 25 cc. of the alkaline tartrate solution in a 400 cc. beaker. Add 50 cc. of the clarified

and neutralized solution above mentioned and heat to boiling in *exactly 4 minutes* and boil for 2 minutes.[1] Filter immediately without diluting, *through asbestos*,[2] wash thoroughly with hot water, then with alcohol, and finally with ether; dry for ½ hour in water oven and weigh as cuprous oxide, determine the amount of dextrose by the use of Munson and Walker's table (Bull. 107: Rev. Bu. of Chem., p. 243) and report in percentage on leather.

(7) *Nitrogen:* Gunning modification of the Kjeldahl Method, A. O. A. C. Bulletin, No. 107 (1907).

REAGENTS.

Standard Acid Solutions.—Hydrochloric or sulphuric acid, the absolute strength of which has been accurately determined. For ordinary work half-normal acid is recommended. For work in determining very small amounts of nitrogen, tenth-normal is recommended. In titrating mineral acid against hydroxide solution use cochineal as indicator.

Standard Alkali Solution.—The strength of this solution relative to the acid must be accurately determined; tenth-normal solution is recommended.

Sulphuric Acid.—The sulphuric acid used should have a specific gravity of 1.84 and be free from nitrates and also from ammonium sulphate.

Sodium Hydroxide Solution.—A saturated solution of sodium hydroxide free from nitrates.

Potassium Sulphate.—This reagent should be pulverized before using.

Indicator.—A solution of cochineal is prepared by digesting and frequently agitating 3 grams of pulverized cochineal in a mixture of 50 cc. of strong alcohol and 200 cc. of distilled water for a day or two at ordinary temperature; the filtered solution is employed as indicator.

[1] The rate of heating of the Bunsen burner used should be regulated before sugar determinations are started. This is best done by adjusting the burner so as to bring 25 cc. copper soln. + 25 cc. alk. tartrate soln. + 50 cc. H_2O in a 400 cc. beaker to 100° C. in exactly four minutes.

[2] The finely divided, long-fibered asbestos to be used in the glucose determination should be digested with HNO_3, washed, then digested with NaOH and washed. When gooch filters are prepared, they should be washed with boiling Fehling's solution, then with HNO_3. The mats thus prepared can be used for a long time.

DETERMINATION.

Place 0.7 gram leather in a digestion flask. Add 10 grams powdered potassium sulphate and from 15 to 25 cc. (ordinarily about 20 cc.) of concentrated sulphuric acid. Place the flask in an inclined position and heat below the boiling point of the acid from 5 to 15 minutes or until frothing has ceased (a small piece of paraffine may be added to prevent extreme foaming).

Then raise the heat and boil briskly until the liquid has become quite clear and nearly colorless (the digestion should take from 4 to 5 hours).

After cooling, dilute with about 200 cc. of water. Next add 50 cc. of soda solution, or sufficient to make the reaction strongly alkaline, pouring it down the side of the flask so that it does not mix at once with the acid solution. Connect the flask with the condenser, mix the contents by shaking, and distil until all ammonia has passed over into the standard acid. The first 150 cc. will generally contain all the ammonia. The operation usually requires from 40 minutes to 1½ hours. The distillate is then titrated with standard alkali.

Previous to use, the reagents should be tested by a blank experiment with sugar, which will partially reduce any nitrates present that otherwise might escape notice.

Provisional Method for the Analysis of One-Bath Chrome Liquors.

CHROME DETERMINATION.

Dilute a measured quantity of the liquor with water to a definite volume so that the dilution contains from 0.15 to 0.25 per cent. of Cr_2O_3. To 10 cc. of this dilution in a 300 cc. Erlenmeyer flask add about 50 cc. of water and about 2 grams of sodium peroxide. Boil gently 30 minutes, adding water if necessary to keep the volume from falling below about 15 cc. Cool, neutralize with strong HCl and add 5 cc. excess. Cool again. Add 10 cc. of a 10 per cent. solution of potassium iodide. After 1 minute run in from a burette 0.1 N sodium thiosulphate until the iodine color has nearly disappeared; then add a few cc. of starch solution (1 gram per liter) and titrate to the disappearance of the blue. One cc. of 0.1 N thiosulphate is equivalent to 0.002533 gram Cr_2O_3.

ACID DETERMINATION.

Place 50 cc. of the above dilution in a 7-inch porcelain dish, add about 400 cc. of water and 1 cc. of a 5 per cent. solution of phenolphthalein and bring to a boil. While boiling, titrate with 0.5 N NaOH until the pink color persists after 1 minute boiling. One cc. 0.5 N NaOH is equivalent to 0.02002 gram SO_3, 0.02452 gram H_2SO_4, 0.01773 gram Cl or 0.01823 gram HCl.

BASICITY.

The basicity is the ratio of basic radical to acid radical, found by dividing the percentage of Cr_2O_3 by the percentage of SO_3 or of Cl, carrying the quotient to two decimal places.

Provisional Method for Analysis of Chrome Leather.

CHROME DETERMINATION.

(a) Ash 3 grams of leather. Mix the ash well with 4 grams of a mixture of equal parts of sodium carbonate, potassium carbonate and powdered borax glass and fuse for 30 minutes. Dissolve the cooled fusion in hot water with enough HCl to make the solution acid. Filter. If there is any residue on the filter, ash it and treat the ash with 1 gram of the fusion mixture in the same manner as the original ash, adding the solution to the first. Make up to 500 cc. To 100 cc. of this solution in an Erlenmeyer flask, add 5 cc. HCl and determine Cr_2O_3 as above in the analysis of one-bath chrome liquors.

(b) If it is not desired to determine Fe or Al, the ash of 3 grams of leather may be transferred to an iron crucible, mixed with 3 grams of sodium peroxide and fused 10 minutes. Place cooled crucible in 300 cc. water in a casserole and boil 20 minutes. Wash into a 500 cc. flask, cool and make up to the mark. Filter through a dry filter. Place 100 cc. of filtrate in Erlenmeyer, neutralize with HCl, add 5 cc. excess and proceed as in (a).

Provisional Method for the Analysis of Sulphonated Oils.

MOISTURE.

Weigh between 30 and 40 grams (depending on amount of water present) into a flask of 250 to 300 cc. and add 75 cc. water saturated xylol, prepared by heating a mixture of water and xylol with frequent shaking and subsequently removing the water in a separatory funnel. Connect to a Liebig condenser and

place flask in a bath of paraffine or a heavy lubricating oil. Distil moderately until the distillate comes clear. Collect distillate in a tube graduated to 1/10 cc. and wash condenser with a stream of xylol from a wash bottle. Place graduated tube in hot water and when the distillate is clear, cool. The percentage of moisture is obtained by dividing the volume of water in the distillate by the weight of oil taken.

NOTE:—For the graduated tube Eimer & Amend's No. 3812 is recommended.

ASH.

Weigh any convenient quantity into a dish or crucible. Ignite gently, allowing the oil to burn and complete incineration until all carbon is consumed.

NON-SAPONIFIABLE.

Weigh approximately 10 grams of oil into an 8-ounce Erlenmeyer flask and add 5 cc. aqueous KOH solution (50 grams KOH in water and dilute to 100 cc.), 45 cc. ethyl alcohol and a few glass beads. Boil 1 hour with reflux condenser. Add 100 cc. water and cool. Transfer to separatory funnel and shake at least three times with petrolic ether (B. P. 40° to 75° C.) using 50 cc. each time. Wash ether layer at least three times with 50 cc. water containing 10 cc. ethyl alcohol. Use alcohol to break emulsion. Evaporate ether extract in tared vessel, cool and weigh.

NOTE:—If the contents of the flask bump violently during saponification add 25 cc. petrolic ether, and proceed.

COMBINED SO_3.

(a) Weigh approximately 4 grams into an Erlenmeyer flask and boil for 40 minutes with 30 cc. HCl (1 : 5). Shake frequently. Cool, transfer to separatory funnel and shake out with petrolic ether. Draw off aqueous layer and wash ethereal layer with water. Combine washings with main aqueous portion and the sulphuric acid determine as barium sulphate. From the amount thus found, the quantity as determined in (b) is subtracted and the difference calculated as SO_3.

(b) Dissolve 4 grams in ether and shake out several times with 25 cc. concentrated brine free from sulphates. Combine the

washings, dilute, filter and determine the sulphuric acid as barium sulphate.

TOTAL FATTY OIL.

The total fatty oil shall be the difference between 100 per cent. and the sum of moisture, ash and non-saponifiable.

NOTE:—The results obtained by these methods shall be reported only in one decimal place.

Provisional Method for Analysis of Moellons.

MOISTURE.

Weigh accurately 3 grams of the sample in a wide platinum dish, and heat with a low flame until the moisture is all driven off. This point can be determined by the appearance of smoke, and a slight crackling sound. Place the dish in a desiccator, cool and weigh.

ASH.

Ash the moellon remaining in the dish after the moisture determination in the usual manner, cool and weigh.

UNSAPONIFIABLE.

Weigh accurately in a 300 cc. flask, 5 grams of the moellon, add 2.5 grams caustic potash dissolved in a little water (or 5 cc. of a 50 per cent. KOH solution), and 25 cc. of 95 per cent. alcohol, boil with reflux condenser for 1 hour, shaking occasionally. Glass beads may be used to prevent bumping. Add 50 cc. hot water, cool, transfer to a separatory funnel, and extract three times. using 40 cc. petroleum ether for each extraction. A little alcohol may be added to break persistent emulsions. Wash the combined ether solutions three times with a mixture of 30 cc. of water and 10 cc. of alcohol, transfer to a tared dish, evaporate to dryness, cool and weigh. Excessive drying must be avoided.

OXIDIZED FATTY ACIDS.

Boil the soap solution remaining from the unsaponifiable determination until all the alcohol is expelled, then dissolve in hot water, transfer to a separatory funnel, rinse the beaker thoroughly into the funnel, bringing volume to approximately 300 cc., and immediately add a slight excess of concentrated HCl (about 25 per cent. more than sufficient to neutralize total alkali). Rotate the contents of the flask vigorously, cool and shake out with pe-

troleum ether. Run off the aqueous layer, and pour off the ether layer, avoiding any loss of oxidized fatty acids. Wash these acids twice with small quantities of petroleum ether and hot water; dissolve in warm 95 per cent. alcohol, filter if necessary, transfer to a tared dish, and place in an ordinary evaporator and dryer for 16 hours; then cool and weigh. The entire operation should be conducted without delay.

FREE FATTY ACIDS.

Weigh out 1 gram moellon, dissolve in mixture of 20 cc. alcohol and 20 cc. sulphuric ether, which has been neutralized to phenolphthalein, and titrate with N/10 NaOH, using phenolphthalein as indicator. Test for mineral acids or alkalies (by adding methyl orange to the water emulsion of the moellon), and if present, make the necessary correction.

Provisional Method for Analysis ef Hard Greases.

TITER TEST.

Saponify 75 grams of fat in a metal dish with 60 cc. of 30 per cent. sodium hydroxide (36° Baumé) and 75 cc. of 95 per cent. by volume alcohol or 120 cc. of water. Boil to dryness with constant stirring to prevent scorching, over a very low flame or over an iron or asbestos plate. Dissolve the dry soap in a liter of boiling water and if alcohol has been used boil for 40 minutes in order to remove it, adding sufficient water to replace that lost in boiling. Add 100 cc. of 30 per cent. sulphuric acid (25° Baumé) to free fatty acids and boil until they form a clear, transparent layer. Wash with boiling water until free from sulphuric acid, collect in a small beaker, and place on the steam bath until the water has settled and the fatty acids are clear; then decant them into a dry beaker, filter, using hot water funnel, and dry 20 minutse at 100° C. When dried, cool the fatty acids to 15° or 20° C. above the expected titer and transfer to the titer tube, which is 25 mm. in diameter and 100 mm. in length (1 x 4 inches) and made of glass about 1 mm. in thickness. Place in a 16-ounce saltmouth bottle of clear glass, about 70 mm. in diameter and 150 mm. high (2.8 x 6 inches), fit it with a cork, which is perforated so as to hold the tube rigidly when in position. Suspend the thermometer, graduated to 0.10° C., so that it can be used as a stirrer, and stir the mass slowly until the mercury remains sta-

tionary for 30 seconds. Then allow the thermometer to hang quietly, with the bulb in the center of the mass, and observe the rise of the mercury. The highest point to which it rises is recorded as the titer of the fatty acids.

Test the fatty acids for complete saponification as follows:

Place 3 cc. in a test-tube and add 15 cc. of alcohol (95 per cent. by volume). Bring the mixture to a boil and add an equal volume of ammonium hydroxide (0.96 sp. gr.). A clear solution should result, turbidity indicating unsaponified fat. The titer must be made at about 20° C. for all fats having a titer above 30° C. and at 10° C. below the titer for all other fats.

UNSAPONIFIABLE.

Same as for Unsaponifiable in Moellons.

FREE FATTY ACIDS.

Same as for Free Fatty Acids in Moellons.

Provisional Method for Analysis of Lactic Acid.

FREE SULPHURIC ACID.

Dissolve 50 grams of the sample in 200 cc. alcohol, which should be neutral, and of at least 95 per cent. strength. Heat to 60° C., cover and let stand over night in a warm place. Filter off precipitated material and wash with alcohol. Evaporate off the alcohol, make up residue to 250 cc. with water, add 5 cc. strong HCl, boil, add $BaCl_2$ and determine $BaSO_4$ in the usual way. Calculated to per cent. H_2SO_4 on the original sample.

VOLATILE ACID.

Weigh out 1 gram of sample, make up to about 50 cc. with water, titrate with 0.5 N NaOH. Calculate the result to lactic acid: (1 cc. 0.5 N NaOH = 0.045 gram lactic acid.) On this basis, make up a solution containing about 15 grams of acid per liter. Place 150 cc. of this dilution in a long-necked 300 cc. Kjeldahl flask, connected through a Kjeldahl bulb trap to a vertical spiral condenser, the total height from the bottom of the flask to the top of the turn connecting with the condenser being between 20 and 24 inches. Distil over 125 cc. in from 47 to 53 minutes, counting from the time the first drop falls into the receiver, which should be a graduated cylinder. Add 125 cc. of

TABLE SHOWING THE RELATION OF AMOUNTS OF VOLATILE ACID FOUND IN DISTILLATE OBTAINED UNDER STANDARD CONDITIONS TO THE AMOUNTS ACTUALLY PRESENT IN DISTILLING FLASK, IN MILLIGRAMS.

One Distillation.

In distillate	In flask	In distillate	In flask	In distillate	In flask	In distillate	In flask
1	0.0	14	17.5	27	37.5	40	57.9
2	0.0	15	19.0	28	39.0	41	59.6
3	0.0	16	20.5	29	40.6	42	61.3
4	2.0	17	22.1	30	42.1	43	62.9
5	3.5	18	23.6	31	43.7	44	64.6
6	5.1	19	25.2	32	45.2	45	66.3
7	6.7	20	26.7	33	46.8	46	68.0
8	8.2	21	28.2	34	48.3	47	69.8
9	9.8	22	29.8	35	49.9	48	71.5
10	11.3	23	31.3	36	51.5	49	73.3
11	12.8	24	32.9	37	53.1	50	75.0
12	14.4	25	34.4	38	54.7	51	76.8
13	15.9	26	35.9	39	56.3	52	78.5

Two Distillations.

In distillate	In flask	In distillate	In flask	In distillate	In flask	In distillate	In flask
5	0.0	22	19.2	39	38.9	56	58.6
6	1.0	23	20.4	40	40.0	57	59.8
7	2.0	24	21.5	41	41.1	58	61.1
8	3.0	25	22.7	42	42.3	59	62.3
9	4.0	26	23.9	43	43.4	60	63.5
10	5.0	27	25.0	44	44.6	61	64.7
11	6.2	28	26.2	45	45.7	62	65.9
12	7.4	29	27.3	46	46.8	63	67.2
13	8.6	30	28.5	47	48.0	64	68.4
14	9.8	31	29.7	48	49.2	65	69.6
15	11.0	32	30.8	49	50.3	66	70.8
16	12.1	33	32.0	50	51.5	67	72.0
17	13.4	34	33.1	51	52.7	68	73.3
18	14.5	35	34.3	52	53.9	69	74.5
19	15.7	36	35.4	53	55.0	70	75.7
20	16.9	37	36.6	54	56.2	71	76.9
21	18.1	38	37.7	55	57.4	72	78.1

water to the residue in the flask and repeat. Titrate both distillates with 0.1 N NaOH and phenolphthalein and calculate result to grams of acetic acid: 1 cc. 0.1 N NaOH = 0.006 gram acetic acid. From these figures for acid found in distillates find actual weight of volatile acid placed in boiling flask, by means of table, and calculate this result to percentage of volatile acid in the sample.

FREE ACID AND ANHYDRIDE.

Titrate 50 cc. of the dilution made up for volatile acid, in the cold, with 0.5 N NaOH and phenolphthalein to first full pink. Call this figure "first titration." From it subtract a number of cc. of 0.5 N NaOH equivalent to the sum of volatile acid and free sulphuric acid present in the 50 cc. of dilution. (If the sample contains free oxalic or hydrochloric acid, the amount must be determined by appropriate methods, and further deduction made.) Calculate the remainder to lactic acid and express it as a percentage of the sample. This is the free lactic acid. After completing the first titration, add 4 cc. excess alkali, or in the case of concentrated acids 5 cc., and stand aside at room temperature (20-25° C.) for 15 minutes. Then add 5 cc. 0.5 N H_2SO_4, boil, and titrate back with 0.5 N NaOH. The amount of alkali used by anhydride is now found by subtraction and calculated to lactic acid. Express this as per cent. of lactic acid equivalent to anhydride present in sample.

Official Form for the Reporting of Extract Analysis.

ANALYSIS.

Tannin	Total Solids ....
Non-tannins	Soluble Solids ....
Insolubles	Ash ....
Water	Specific Gravity ....
Total	Twaddell ....

Analyzed by the Official Method of the A. L. C. A. { SLOWLY / RAPIDLY } Cooled.

JAPANESE WHITE LEATHER.*

By Lloyd Balderston.

The white leather industry of Japan centers about Himeji, a city of some 300,000 inhabitants about 50 miles west from Osaka.

The village of Takagi, which has been making white leather for 300 years, has a population of about 3,500, living in 600 houses, occupying a space of hardly more than ten acres. It is said to be like a piece of China, set down in the midst of Japan, and to the Japanese the villagers have a different look from other

* Reprinted from *Shoe & Leather Reporter*, Sept. 25, 1919.

people. They were of the "eta" class in the old days. This class was the lowest, socially, and certain occupations, including leather making, were carried on by eta only. They were meat eaters in the old days when Japanese generally did not eat meat. The name eta has no official recognition in Japan now. The late Emperor early in his reign abolished the eta class and promoted them to be "hemin", ordinary people. But I notice that the term "shinhemin" is in use, which means "new hemin", so there is a distinction, whether any difference or not. Whatever the social handicap of the people of Takagi may be, they make a very useful product, which nobody has succeeded in imitating.

The village is not attractive in appearance. The wide streets are 8 feet from wall to wall ,with a gutter on one or both sides. The narrow ones are as little as three feet in width, and are simply gutters, in which you pick your way on the loose stones. Winding along one of these we came to the gate of a Handsome temple!

This little place furnishes nearly all of the $150,000 worth of white leather produced annually in Japan. The industry is essentially a domestic one, in which practically all of the people old enough to work are engaged for at least a part of their time. If attractive wages are offered in factories or on farms, they will do something else for a while, but when other tasks are not pressing, there is always leather making to do. The tools required are few and inexpensive, and but little space is needed for the part of the work which is done indoors. Much of the capital invested in hides comes from Osaka or elsewhere.

The river is swift, and the main current flows along an outer curve past the village. The slope of the river bank is perhaps 50 yards wide, and it is gridironed with ridges at right angles to the stream. These are a foot high with a steep side toward the north and a gentle slope some eight feet wide facing the south, forming a sort of sloping terrace, built of pebbles. These ridges number a hundred or more, and on a sunny day they will be covered with hides, loosely spread out, grain side up. Japanese white leather, like hay, must be made while the sun shines.

I have met with but two accounts of the process in English, both of them abstracts in the third volume of the JOURNAL OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION, 1908. Both are

from *Gerber*. The first, page 92, is by W. Eitner, on the authority of F. Reinhardt. The facts in this are nearly correct as far as they

Foreground : Hides spread to dry and bleach. Middle distance, fleshings drying.

go, but some of the inferences seem to me quite unfounded. The name of the village is given as "Jakayimura" instead of Takagimura. (Mura is Japanese for village). This error is obviously

due to misreading manuscript. The name of the river is also somewhat modified. The only statement of Mr. Reinhardt's which I question relates to the oil used in making the leather. He says he extracted a small percentage of a non-drying vegetable oil, which has no tanning property. The oil used is from rape seed, and it is classed by Lewkowitsch as a semi-drying oil.

The other abstract is from a paper by Professor Toyomaru. In this the oil used is said to be cotton seed oil. This is certainly a misstatement, which is probably due to wrong translation of the Japanese word for rape seed. The name Himeji appears as "himesji", an adjective describing the leather.

Mr. Sawayama is contributing a series of articles on this leather to the Live Stock Journal, published by the Hokkaido Live Stock Association. A few of the points which follow are taken from the first of these papers, but nearly all my information was obtained direct from Mr. Sawayama, and through him from Mr. Kitanaka, who has been familiar with the manufacture for a long time. I saw all the processes, some on the river bank, some at one house, some at another ,but could only connect these up through outside information.

Any kind of hide will do. Japanese green or wet-salted hides are used to some extent. We saw one freshly flayed cow-hide being brought in to be put in process. The great majority, however, are dry or dry ?salted hides of rather inferior quality. This is possible because most of the uses to which the leather is put are such as not to demand large pieces without blemish, and on the other hand the price which the product commands is too low to warrant the use of high grade stock.

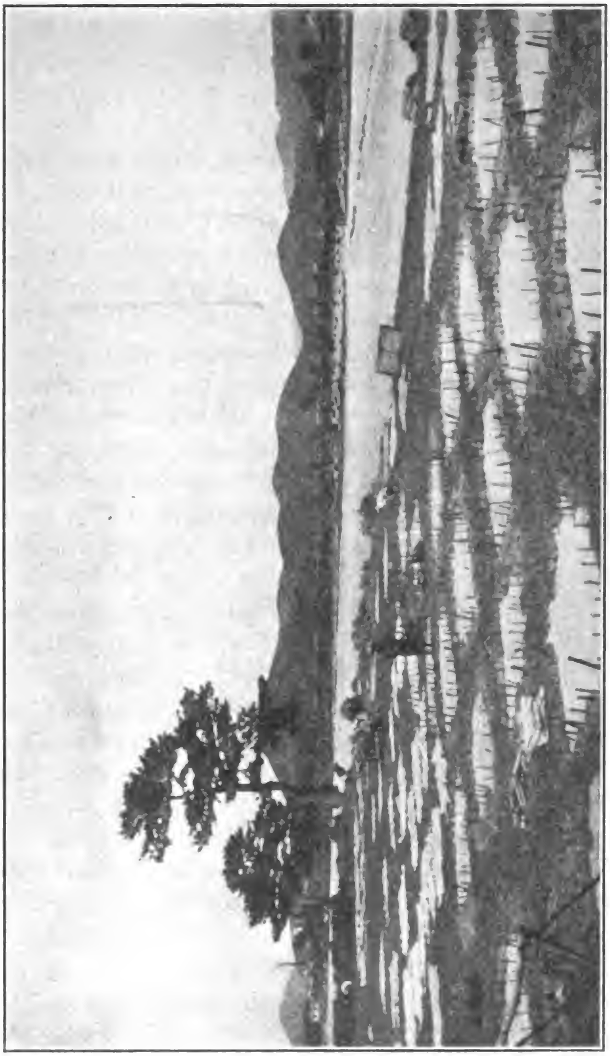
The first process is to tie the hides by ropes to stakes set in the river, in water one or two feet deep, in such a way that they float out and wave up and down in the current. The water must be clear and not too warm, so in summer this soaking is done in a branch of the river coming down out of the mountains which is cooler than the main stream. The time required for the hair to be ready to slip is in summer 3 days for fresh hides, 4 days or more for dry or dry-salted ones. In spring and fall these periods are longer ,ranging perhaps from 10 to 14 days. In the fall the hides are often taken out of the water and laid in pile covered with mats for a few days to "sweat" before the hair will slip. In

winter this first soaking may take a month. The unhairing is done on a flat board, the worker standing up, the board with the hide being on the ground. The hair is pushed off with a tool consisting of a slightly curved blade fastened spade-wise to a handle four feet or more long.

The man is standing on a hide which is in the treading process. Many others are folded and piled behind.

The next process is a brief washing. The hides are then shaved to the required thickness on a flat cherry plank about 14 inches wide sloping about 30 degrees from the horizontal, with a knife built much like an American "spoke shave" except that the very thin blade is at right angles to the face of the tool. This tool is pushed, not pulled. It takes about 40 minutes

to shave a skin. The material shaved off is dried in cakes about 12 by 16 inches in size and an inch thick and sold for glue stock.



Final Stage. Hides pegged out to dry.

The wet shaved hides are now sprinkled with salt, from one and a half to three quarts, depending on the size of the hide. The hide is now trodden and worked with the bare feet to work in the

salt. This is done in a shallow wooden tub. The color becomes lighter as the salt penetrates, and this color change is the index of the completion of the process, which requires 15 minutes or more for one hide. The hides are now packed into a cask where they lie for from one to three days for the salt to become uniformly distributed. During this period the grain is liable to become mottled by the growth of some organism on the surface.

The next step is to spread the hides out in the sunshine to dry and begin the bleaching process. If the sun is not shining, they are trodden every day until it does, to prevent mottling of the grain. The period of exposure to sunshine required for this first drying and bleaching is sometimes as short as two or three days in dry warm weather, but in winter it may reach thirty days. The completion of this stage is judged by the appearance of crystals of salt on the grain side. To decide when the proper condition is reached is one of the most difficult points in the whole process.

The next stage may be translated as "seasoning", but the term is rather contradictory, as it consists in the removal of salt by soaking. In summer this is done by immersion in the river, but in cool weather the hides are placed in water in a cask. The proper length of soaking to leave just enough salt in the skin is determined by tasting. After drying, the hide is ready to receive the rape seed oil which is the chief agent in the actual tannage. The surface is prepared to receive it by spraying with water blown from the mouth, as the Chinese laundryman used to sprinkle clothes. The oil is applied to the flesh side with a swab, from 2 to 5 ounces per hide, depending on size and thickness. Marine animal oil may be used instead of rape, but the color of the finished leather is not so white as that made with rape oil.

A number of holes are now cut around the edge of the hide, and a string run through, making a bag of it, grain side out. This is so folded as to make a mass two feet or so long, and the second treading process begins.

This time the hide rests on a straw mat on the floor. The worker grasps a horizontal bar and kneads the hide with his bare feet, much as the housewife used to treat dough with her hands. I suppose there is some Japanese term to denote foot skill as dexterity describes skill of the right hand, and that it is applied to the deft movements by which the soft mass is worked over

and over until the oil comes through to the grain side. This work is done by men, women and half-grown children. The warmth of the feet is an essential element in it. The time required is from a half day to a day or more, depending on the size of the hide and the weight and strength of the worker.

A light coat of oil is now applied to the grain side, and another shorter period of treading follows. Next comes a second period in the sun, shorter than the first, and depending on the weather as before. Another treading follows, a little oil and water being applied if needed. The next step is to wash with a little water, to avoid loss of salt. The hide is spread on a horizontal board and a wisp of straw is used as a brush. If the hair did not come off entirely in the first place, remaining patches are now removed by shaving with a knife, and another period of drying and bleaching follows, covering three days or more.

Another treading comes next, then a first staking, about 15 minutes to a skin . The staking tool is of the familiar pattern, but the upright is not high enough for a Western man to work at with comfort. Another period in the sunshine follows, then another treading, the grain inside this time, and then another staking.

Now follows a long period of bleaching in the sun, 40 days in winter, but sometimes as little as 4 in summer. The color at the end of this period is white, the yellow due to the oil having been entirely bleached out. After this the goods lie in pile, folded, for from 30 to 60 days, depending on the time of year. (The temperature reaches the freezing point only a few times in the course of the winter in Himeji.) During the piling the oil comes to the surface again, but a few hours' bleaching restores the white color.

A short soaking to remove more salt is now given, the proper point being determined as before by tasting. This results in bringing back the yellow color again. Another washing with a wisp of straw is followed by sunning for about a day. The leather is now rather hard, the grain side smooth, hair pattern hardly showing. The flesh side is somewhat yellow. Each hide is now folded in four and placed in the river until just wet through, then trodden and staked, then laid in the sun for half an hour, and while warm from the sunshine trodden again for

half an hour and staked for half an hour. The skin is now quite white and the hair pattern shows plainly.

Another sunning of from one to three hours is followed by another treading and another staking. The hides are now spread out on the ground over night to become damp, and are then pegged out on straw mats on the ground, stretched as tightly as possible, being exposed to the sun for the final drying. The whole time consumed in the process averages about six months.

The product is as soft as well bated side leather, as tough and durable as oil-tanned lace leather and as white as the whitest alum-tanned leather. It is divided into three grades with respect to thickness, and these are subdivided into grades of both quality and weight. The heavy grade averages 35 pounds per 100 square feet, present prices ranging from 51 to 65 sen per square foot. The actual measure used is the square shaku, which is about 0.99 of a square foot. The sen is about half a cent. Medium weight ranges around 25 pounds per 100 square feet, and brings from 59 to 62 sen. Light weight averages 17 pounds per 100 square feet and brings from 57 to 60 sen. The grading is done at the request of exporters, the pound used being the same as ours. Quality is not very uniform, there being too many factors difficult to control.

The heavier grades are mostly used in Japan, largely for straps of various kinds, lacings for fencing armor, belts for light machinery, etc. The best quality wooden clogs have white leather straps. Export trade takes the lighter skins. These are used for suspender tabs, bags, purses and fancy articles of various kinds. The low prices above quoted are made possible by the fact that the hides used are cheap, and the further facts that the expense for materials is very small, that the glue stock commands a steady market at a good price, and most important of all, that the labor is very poorly paid. Tanneries elsewhere are beginning to draw upon the skilled resources of Takagi, and this fact cannot fail to have its effect on the conditions of work here. Certainly it is greatly to be desired that such a laborious manufacture should be rewarded by better prices being obtained for the white leather.

Many of the hides we saw were seriously defective, full of warble holes, "sunburned" or otherwise injured. One was branded "C C", apparently a Mexican hide. The same kind of

leather is made at two other villages near Himeji, but is not so good as the Takagi product. The difference is attributed to slower current in the stream and lower purity of the water. At Osaka and Kobe it is impossible to make it because the air is so full of soot that anything laid out in the sun becomes dirty beyond recovery.

It has been suggested that the production of this leather is in some way promoted by the character of the water. Such an explanation is very improbable. The country has heavy rainfall, and the Ichikawa is a short and rapid stream of high volume. Under such circumstances the presence in the water of any mineral matter having tanning effect is not likely. The mere fact that when the water is moderately warm hides immersed in it slip their hair in a few days shows that it is not a tanning agent.

I believe that this famous leather is simply oil-tanned with the minimum of oil and the maximum of labor. In the first place, about 5% of salt is worked in, and this produces a sort of temporary tannage. It is a familiar fact that a salted hide is not flint hard. The working in of the oil is very thorough, and as it slowly produces its tanning effect, the salt is gradually worked out. In the ordinary kind of oil tannage, a great excess of oil is used, and afterward removed. There is no more free oil in chamois than in Japanese white leather, and it is possible to bleach chamois almost white by exposing it to the sun in a damp condition. If a split cowhide was subjected to chamoisage with rape-seed oil and then sunbleached, it would probably be much like Japanese white leather. I intend to try some experiments along this line, but shall be glad if other leather men will do the same, especially if they will publish their results!

LEATHER DYEING.*

By Louis G. Hayes.

The dyeing of leather is generally carried out by one of two methods, either by brushing a solution of the color on the leather or by drumming in the paddle-wheel. Of these two methods the drumming is considered the best, as larger quantities of material may be handled, the results are more uniform, and much

* Condensed and reprinted from *Col. Tr. J.* 5, 108, (1919).

better penetration of the leather is obtained. Where only the grain of the leather is to be dyed, or where a ground shade is dyed in the drum and a different color is wanted on the grain to complete the effect, or where cowhide splits are to be colored, naturally the brushing method is preferable. The tannage of the leather governs the choice of dyestuffs employed, and therefore it will be best to consider the differently tanned leathers as classes and to give the kinds of colors used on each.

The dyestuffs employed for leather dyeing are divided into six distinct groups, namely:

1. Basic colors, which have their greatest use in the dyeing of vegetable tanned leather or on chrome leather with a mordant of some tannin containing material. They are also used in the coloring of a great many leather finishes and polishes.

2. Acid colors, which may be applied to either vegetable or chrome leather and have great penetrating powers.

3. Direct colors, known to the trade as diamine, or naphthamine colors, and benzo colors, which are mainly used on chrome tanned leather, and in some instances on vegetable tanned leather.

4. Mordant colors, such as alizarine colors, chrome or anthracene colors. This class is seldom used owing to the fact that most colors of this group require a boiling temperature to develop the shade, a process which is impossible in the case of leather. A few of them, mostly the yellows, have been successfully employed on chrome leather and yield shades that are extrmely fast to light.

5. Dyestuffs which are diazotized and developed on the fibre, such as Primuline, Diamine Black BH, Diazine Black H, etc. This class of colors is used only on chrome leather and while fancy shades may be dyed by this method, it is seldom used except for the production of blacks, which yield full blacks on ooze leathers.

6. Sodium sulphide colors, Immedial, Thion, sulphur colors. These colors are only applied on chamois leather, the uses of which make it essential that the coloring matters employed should be fast to washings.

Other types of colors are the oil colors, such as the cerasine colors that are employed a great deal in the coloring of the waxes used in the finishing of leather. All of these colors and their ap-

plications will be more fully taken up under the special classes of leather.

Under this head come three different classes:—

1. Sumac tanned sheepskins
2. Quebracho tanned sheepskins
3. India tanned sheepskins

also the corresponding types of goatskins and the various tannages of cowhide, known as side leather.

Basic colors are most generally used on this kind of leather and they yield extremely bright shades but these shades are not fast to light and are poor to rubbing. Since in the majority of cases the leather is given a heavy coating of some protective finish which generally contains a great deal of wax or other such material, this latter fault is to a considerable extent obviated. The Phosphines, the various brands of which yield a yellowish or a reddish shade of tan are very fast to perspiration and are used extensively in the dyeing of saddle leather. Phosphine, Thioflavine, Bismarck Brown, Methyline Blue, Safranine, and New Blue or Fast Indigo Blue are among the fastest to light of this group of colors. However, all of the basic colors have a great affinity for vegetable tanned leathers and their choice is governed by the shade to be matched and the requirements of the same.

Acid colors are also used extensively on vegetable tanned leather but they are seldom used for self shades except in the production of very light shades where the necessity of level dyeing is essential. Their other desirable properties are that they have great penetrating powers and that certain brands are extremely fast to light. Their greatest use is for a bottom shade, after which the leather is dyed with basic colors to give it fullness and brightness.

The acid colors which are mainly used for the production of light shades are as follows: Acid Yellow AT, which is Tartrazine, Orange II, Lanafuchsine SB, Ajanole FF, and Cyanole Fast Green G. For the deeper shades the colors most frequently used are: Azo Yellow, Metanil Yellow, Orange II, Scarlet EC, Brilliant Croceine Scarlet, Bordeaux BL, Acid Violet, Brilliant Milling Blue, the Pure Soluble Blues, Solid Blue, Acid Green, Alizarine Black, Napthol Black and Napthol Blue Black. One

of the great drawbacks to the use of acid colors on vegetable tanned leathers lies in the fact that they bleed badly in the fat-liquoring process and although various means of application have been tried it has not been overcome. The direct colors are very seldom used on this class of leather owing to their poor affinity.

After the skins have been thoroughly tanned and have been "trimmed" they are then weighed and sent to the dyehouse with a tag showing their weight, which is called "shaver's weight," attached. One of the most inportant things for the leather dyer to observe is the cleanliness of his skins and to see that all surplus tanning material is removed. With these facts in his mind he must weigh his batch of skins and put them into the "drum" with warm water at about 110° F. After drumming for fifteen to twenty minutes the skins are now ready to dry.

In the case of sumac tanned skins which are very light in color it is not necessary to give any preliminary treatment, but even in this case, if the shade to be dyed is a delicate one, it will be found better to first give the skins a drumming with ¼ to ½ per cent. of tartar emetic which fastens on any surplus tannin and gives a clear bottom. This treatment is also used after dyeing with basic colors as it fixes them and improves their fastness to the fat-liquor. For tan shades or other darker tones the skins are given a treatment with titanium potassium oxalate which produces a yellowish tone on the leather at the same time fixing the tannage. Bichromate of potash is very often used after the dyeing where an extremely fast shade is wanted or as a saddening agent instead of blue. After the skins have been cleared and given whatever preliminary treatment is considered best they are put in the drum, the proper amount of water at 110-120° F. added and the drum started. The dyestuff which has been well dissolved is then added in two or three parts through the hollow axle of the drum, and drummed until the dyebath is exhausted. In the case of acid colors it may be necessary to add a little sulphuric or formic acid to help the exhaustion, but this method is dangerous as it has a tendering effect on the leather when stored. When the dye liquor is well exhausted the skins are allowed to drain in the drum and are then fat-liquored. This is generally done with an emulsion of neatsfoot oil or some other oil with soap, and the addition of flour and dried eggyolk.

To make this process clear it is best to give a working formula, the following being for a light tan produced on bark tanned sheepskin:—

(For 100 lbs. bark tanned or quebracho tanned sheepskins, shaver's weight).

The well-cleaned skins are bottomed in the drum with: 3 lbs. sumac extract at 120° F. for 30 min. after which 4 oz. tartar emetic is added to clear them. They are run 15 minutes longer then allowed to drain. 5 oz. Tropaeoline R. N. P. is then added in a fresh bath, run at 120° F. for 20 minutes and drained. The skins are then topped in a fresh bath with:—

1 lb. 5½ oz. Basic Phosphine
6½ " Bismarck Brown
¾ " Methylene Blue

and run 30 minutes at 120° F. or until the dye liquor is exhausted after which they are drained and topped in a fresh liquor with:—

1½ oz. Safranine, yellow shade

and run at 120° F. until exhausted.

The skins are then "set out," oiled off on the grain, and tacked out to dry. When dry they are staked and seasoned with a weak albumen solution.

This seasoning is done in the following manner. A season is made up as follows:

1 oz. of soap is dissolved in 1 gallon hot water.
2 oz. gelatine are stirred into it, dissolved and then cooled.
8 oz. egg albumen or blood albumen for darker shades is dissolved in 1 gal. cold water and then added to the first solution. One pint of milk is then added and the entire quantity made up to 3 gallons.

This solution is then "swabbed" onto the grain of the leather and allowed to dry, after which the skins are ready for glazing. This is done by means of a glass roller held in the "jack," which resembles a huge arm drawn over the leather with great pressure and friction. The operator of the machine moves the skin around until all portions have been evenly glazed. This glazing produces a very high polish. For the most perfect glaze a skin with a hard grain is essential and since goatskins have this property especially they are used extensively for this class of leather.

Black and tan shades, which are of course the most frequently used shades for this leather, are generally dyed by one of two methods. The first is to dye them directly as follows: The weighed skins are drummed with 2 lbs. Nerazine or Nigrosine (per 100 lbs. of skins), either jet shade or bluish according to the shade desired, for 30 minutes after which they are drained and topped with ½ to 1 lb. of Leather Black of which there are many on the market, or a suitable combination of basic colors such as Methylene Blue, Solid Green, Methyl Violet and Bismarck Brown or Chrysoidine. The skins are then fat-liquored, dried, seasoned and finished in the regular manner.

The more frequently used method is the one in which logwood, either crystals or more often the extract, plays an important part. The logwood, aside from acting as a coloring matter, also has the property of acting as a tannin and imparts firmness and body to the leather.

Two lbs. logwood extract (per 100 lbs. of wet bark tanned skins), and ¼ lb. soda ash are drummed for 30 minutes at 120°-130° F. and are then struck with: ¼ to ½ lb. ferrous sulphate (copperas) and run an additional 15 minutes, after which the skins are drained and dyed with either 1 to 2 lbs. of Leather Black, or are topped with 1 to 2 lbs. of Nerazine, then run 30 minutes at 120° F. and fat-liquored in the usual manner.

In all the formulas mentioned it will be noticed that the tannin-containing materials such as fustic, sumac and logwood have been applied as a bottom, but this is not to be construed as the only times that they are used as they are very often added at the end of the dyeing operation, that is, after the aniline colors have been applied.

While the three preceding recipes are for dark or medium shades it may be interesting to have a formula for a few of the lighter and fancy shades as grays, pastel shades, etc. Since the following recipe is for a gray on bark tanned ooze leather it may be well to devote a few paragraphs to the explanation of this kind of leather and the methods of manufacturing it. Ooze, velvet and suède leather are all synonymous, being merely the different names under which this particular leather is known.

Skins which are damaged on the grain side are generally chosen for this class of leather. A perfect grain is non-essential since

the leather is finished on the flesh side. No skins which are marked with slaughter cuts due to careless skinning can be used, however, as they will, of course, show badly in the finished product.

The tannage is practically the same as in the case of the other light skins and both the vegetable and chrome tannages are used. The process begins to differ after the tannage, however, when the skins are put for 30 minutes into a clean, dry drum with three pounds of powdered pumice in order to smooth the flesh side and to cut the longer pieces of stringy leather. The skins are then taken out of the drum and are "cut" over a wet carborundum wheel on the flesh side so that all the fibres are uniformly fine over the entire surface of the skin. After this process the skins are very thoroughly washed to remove all the traces of powdered pumice and are ready to be dyed. It is readily apparent that for this kind of leather one of the essential requirements of the dyestuffs employed should be their penetrating powers so that no light spots should be discernible in the finished skin. Also the level dyeing properties should be borne in mind.

The particular recipe which follows is for a bark tanned ooze leather, but chrome tanned ooze is also very popular and will be taken up subsequently in the chapter on the dyeing of chrome tanned leather.

The skins are first washed with (per 100 lbs. skins, wet weight) 2 lbs. bicarbonate of soda, to partly strip the tannage and run 30 minutes at 120° F. after which they are washed and drummed with 8 lbs. dry sumac, which is dissolved and then added through the hollow axle of the drum and run for 30 minutes after which 12 oz. copperas, ferrous sulphate, is added and the skins run an additional 15 minutes after which they are washed and dyed with 2 oz. Nigrosine, jet shade, water soluble, run for 20 minutes at 120° F. and allowed to drain.

Should the shade desired be duller or flatter another addition of 4 oz. copperas should be made and the skins drummed a further 20 minutes after which they are ready to be fat-liquored. Any fat-liquor may be used, the essential point being that it should be of such a nature that no free grease should adhere to the skins. They must be perfectly dry when finished to have the nap of the right "feel." After fat-liquoring the skins are lightly set

out, oiled slightly on the grain side only and tacked out on the boards to dry. While they still contain a small amount of moisture they are taken from the boards, put into a dry drum and milled for 1½ to 2 hours, to raise the nap which has become flattened during the dyeing operation. They are then lightly staked and run over a velvet wheel as a final treatment. For the darker shades such as tans, greens, blues and blacks, it is always advisable, after cleaning the skins with one of the chemicals previously mentioned according to the shade to be obtained, to give a bottom color of some suitable acid color which will penetrate the fibres well, and then to top with a small amount of basic color to give body and brilliancy to the shade. It is needless to say that any variety of shade may be produced by the variation of colors.

In the production of pastel shades there must be taken into consideration the great danger of unevenness in the dyeing, owing to the difference in the skins. It will be found that the various portions of the individual skin take up the dye differently, as for instance the "butt," or the back portion will be a shade or two deeper than the "shanks" or legs. For these shades, which are generally very bright and delicate, the vegetable coloring matters which would be ideal for this kind of work are far too dull and therefore the acid colors are used exclusively. The general custom is to dye the color desired several shades deeper than is necessary and then to lighten or bleach, as it is sometimes called, by first treating the skins in a bath of ½ per cent. of sugar of lead, lead acetate, and then without rinsing, giving a bath with a small amount of sulphuric acid. This treatment deposits the very minute particles of white lead sulphate evenly throughout the leather and may be repeated until the desired shade is obtained.

Another method of producing these shades is by dyeing the skins with acid colors with the addition of sumac extract and a soluble oil to the dyebath to retard the dyeing operation. Very good results may be obtained in this manner. This method is used by a great many manufacturers in preference to the bleaching method as no sulphuric acid is necessary against the use of which there seems to be a strong prejudice. Any of the acid colors will be found suitable for this work, the following being

the most preferable: Tartrazine, Orange II, Azo Fuschine 2B and 6B, Cyanole FF, Cyanole Green B.

Bark tanned side leather, owing to its size is generally dyed by the brushing method, but since it is now possible to split the sides on the splitting machine, they are also dyed in the drum. When such is the case the same procedure as is used in the dyeing of smaller skins is followed. If the skins are to be brush-dyed two classes of colors are used, either the basic or acid colors, or a combination of the two. The sides are generally spread on a table or bench and then swabbed over with the dyestuff which has been previously dissolved, giving as many coats as are necessary. When the sides have been tanned with a tannage that leaves a rather dark bottom it is found very advantageous to brush a weak solution of sumac over the skin giving a lighter color and assisting in producing level shades as well as wetting out the leather. It is usually wet out with this weak sumac decoction or by brushing with water and is then ready for dyeing. The dyestuff should be made up of such a strength that it will require two or three coats to produce the desired shade and in this way the possibilities of uneven results are reduced to a minimum. In the last brushing it is customary to add whatever finishing dressing may be necessary. A typical working example of this type of dyeing would be the familiar side leather with the blue back and black grain. The sides are first dyed in the drum either with one of the Solid Blues or Indulines which produces the blue shade. Then after drying they are brush-dyed with a basic black of which there are many brands; or this black may be made up by mixing the proper proportions of Bismarck Brown, Methyl Violet, Victoria Green and Methylene Blue or some such similar combination. For this class of work in which penetration is of little importance it will be found much more economical to use the basic colors which have much greater tinctorial powers and produce far more brilliant shades. The Nigrosines and Nerazines are also much used for this work and yield blacks with a bluish tone.

The oil colors known as fat colors or Cerasine colors come into consideration for this work also. They are dissolved with the dressing and applied at the same time that the leather is stuffed with whatever oil is necessary. Brush-dyeing is rarely resorted

to for the coloring of anything but heavy leathers except in the production of fancy antique or marbled leathers.

The Dyeing of Chrome Leathers.

As stated before this kind of leather is made by a strictly chemical process. On chrome leather all three classes of colors are used, namely, acid, basic and direct, and these are chosen with the fastness of the ultimate shade in mind. The acid colors, which may be dyed directly without the addition of tannin materials are the ones which yield the most level shades, have the greatest penetrating powers but are poor as a rule to fat-liquor. If these colors are given a topping in a fresh bath with basic colors which form a lake with the acid colors they are then much faster to the acid fat-liquoring process. The acid colors most frequently used are as follows:

For Yellow: Tartrazine, Fast Light Yellow 2G, Milling Yellow O, Azo Yellow, Metanil Yellow, Resorcine Yellow, and the Tropaeoline brands.

For Orange and Brown: Orange II, Orange GG, Croceine Orange, Tropaeoline, R.N.P, Acid Brown D, Havana Brown S, or Resorcine Brown. For brown, combinations of yellow, orange, and Napthol Blue Black.

For Red: Fast Red A, Bordeaux B L, Wool Red B, Napthol Red C, Ponceau and Brilliant Croceine, and Azo Rubine.

For Blue: Solid Blue R, Brilliant Milling Blue B, Soluble Blue, and Nigrosines, Blue shade water soluble.

For Green: Acid Green extra concentrated, Brilliant Milling Green B, Napthol Green B, and Cyanole Fast Green G.

For Violet: All brands of Acid Violets and Formyl Violets.

For Black: None of the Acid Blacks yield what may be called a really full black on chrome leather, serving only as a bottom color or as a shading color. The ones most frequently used are Napthol Black, Napthol Blue Black and Napthylamine or Alizarine Black. Nigrosine jet shade yields, however, a good black but is not very fast to alkalies. Most tanneries are still much in favor of having a vegetable tanning material on the skin as it undoubtedly assists in producing a better leather. This material, which is generally sumac and gambier for light shades, and logwood and fustic for heavier shades, may be applied either before or after the dyeing operation

The diamine colors, benzo or naphthamine colors have come into importance for use on chrome leather and recently they have been recognized as producing full, bright shades which have ex-

ceptionally good fastness to light and rubbing. These properties are accentuated by an after-treatment with chromium compounds or bluestone (copper sulphate.)

Beside producing fancy shades of very good fastness, the direct blacks are fast replacing logwood and the basic blacks, for the production of blacks on both chrome tanned calf and goat skins. The dyeing operation is measurably shortened and the shades are far faster to light.

The direct colors of most importance for this leather are:

For Yellow: Diamine Fast Yellow B and FF, which are the same as Naphthamine Yellow NN and BN, Chrysophenine, Diamine Fast Yellow A, which corresponds to Stilbene Yellow.

For Orange: Diamine Orange G, Toluylene Orange, and for extremely fast shades, Diamine Fast Orange EG and ER.

For Red: Congo Red, Benzo Purpurine. When these two colors are used the leather should be very carefully neutralized as they are very sensitive to acids. Also Diamine Fast Red F and 8BL, Diamine Fast Bordeaux.

For Browns: Diamine Brown G and 3G and all the Diamine Catechine brands. Napthylamine Brown 2GX, Erie Fast Brown 3RB.

For Blue: Diamine Blue 2B, Diazine Black, Diamine Fast Blue FFB and Naphthamine Brilliant Blue G and R.

For Green: Naphthamine Green AG and AB yield full deep greens.

For Black: The Oxydiamine Black brands. When dyeing with the direct colors special attention should be given to the perfect neutralization of the skins, as most direct colors are precipitated by an excess of acid and work much better in a slightly alkaline dyebath.

These colors exhaust excellently, produce shades which, compared with the acid and basic colors, are extremely fast to light and, when topped with basic colors, produce shades which have the brilliancy of direct basic dyes with the fastness much improved. As stated under the acid colors, tannin is very frequently used, but in the case of direct colors it should be applied after the dyeing. The tannins retard the dyeing of these colors, and therefore the dyebath is not thoroughly exhausted, with the resultant loss of dyestuffs.

The basic colors have little or no affinity for chrome tanned leather and are never used for self shades without previously retanning the skins with a vegetable tannin chosen with due re-

gard to the shade desired. A vegetable tannage is not necessary, however, when the skins have been first dyed with direct or acid colors and a small quantity of basic color only is used. A color lake is formed between the basic and direct or acid colors. All of the basic colors are applicable to leather treated as before stated and those fastest to light are the Phosphines, Thioflavine, Bismarck Brown, Safranine, Methylene Blue and Fast Indigo Blue. The colors which have the greatest penetrating powers among this class are Auramine, Chrysoidine, Fuchsine, Methyl Violet and Malachite Green. These colors also are made much faster to fat-liquoring and light when after-treated with bichromate of potash, tartar emetic, bluestone or potassium titanium oxalate. These after-treatments, however, sadden the shade materially and this fact should be borne in mind when using these compounds. It is the opinion of the writer that a more intimate knowledge of the application of these various groups of dyestuffs and their combinations can be obtained by giving working formulae. With this in mind I will give formulae which have been worked out in practice on various shades.

On most light shades on chrome tanned leather with the exception of light blues, pinks, lavenders and greens, the shades are mainly produced with combinations of the dyewoods and various "strikers," as chrome, bluestone, titanium oxalate and copperas, and just enough dyestuff to give the skins the proper amount of brilliancy. The dyewoods alone leave a dull appearance on the leather. For the other light shades above mentioned acid colors are used entirely and it would be almost impossible to obtain level shades with these colors alone. A typical example is as follows: Light Green on Chrome Tanned Ooze Leather. (Per 100 lbs. of skin; wet weight). Two oz. Napthol Green B, running the skins ½ hour. Allow to drain and then treat the skins in successive baths of lead acetate and sulphuric acid moving them from one bath to the other without rinsing. By this treatment a fine, white precipitate of lead sulphate is evenly distributed throughout the fibres of the skin, lightening the shade. This process is continued until the desired shade is obtained after which the skins are fat-liquored and dried in the customary manner.

For light sand shades and the so-called putty shades an entirely different procedure is followed. Here the dyewoods are utilized to produce the largest part of the coloring.

(Per 100 lbs. chrome tanned calfskins, wet weight.)

5 lbs. sumac extract; run 45 minutes at 130° F., drain and strike with 2 lbs. ferrous sulphate, run 15 minutes, and wash thoroughly.
1 lb. quebracho extract.
8 oz. fustic extract, run 30 minutes at 130° drain, and dye with 1½ oz. Phosphine.
½ oz. Bismarck Brown, run 30 minutes at 130° F., drain and finish in the customary manner.

Another of the fashionable shades is a light gray which may be produced successfully as follows:

(Per 100 lbs. chrome calf, wet weight.)

5 lbs sumac extract, run 30 minutes at 130° F., add
2 lbs. 8 oz. ferrous sulphate, run 30 minutes, rinse well and dye with 2½ oz. Nigrosine, jet shade.
1 oz. Phosphine, run 30 minutes, drain and fat-liquor with 11 lbs egg yolk.
3 lbs. acid fat liquor. Run 30 minutes, drain, and tack out to dry.

While these formulae may seem antiquated, the writer has found that they produce shades which are perfectly level and have excellent penetration, thereby giving the leather an appearance of fullness and body.

The next formula, which is for a tan shade, describes the use of both direct and basic colors and produces a shade which has extremely good light fastness.

(For 100 lbs. chrome calf, wet weight.)

1½ lbs. Diamine Orange D.
4 oz. Bordeaux B.L.
½ oz. Diamine Fast Blue FFB, run 30 minutes, drain, and treat with 2 lbs. fustic extract.
1 lb. cube gambier, run 30 minutes, drain and dye with 1 lb. Phosphine.
1 oz. Bismarck Brown, run 30 minutes, drain and strike with
4 oz. bichromate of potash, drain and fat-liquor with
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11 lbs. egg yolk.
3 lbs. acid fat liquor, tack out and dry.

For the production of black on chrome-colored leather the direct blacks have come into great favor owing to their great covering properties. Their one objection, however, as with all direct and acid colors, is that they leave the leather harsh and therefore it is advisable to use some logwood to "fill" it.

(Per 100 lbs. chrome tanned calfskins.)

1 lb. logwood crystals are dissolved with 4 oz. sal soda and the skins stained in this for 30 minutes, drained and dyed with
1 lb. Oxydiamine Black
4 oz. sal soda
4 lbs. common salt. Run ½ hour, and fix with
2 oz. ferrous sulphate. Run ¼ hour, rinse, drain, and then fat-liquor in the customary manner.

Another means of obtaining an excellent black or chrometanned ooze leather which was gaining in favor just before the outbreak of the war was produced by the use of diazotizable colors. A recipe follows:

(Per 100 lbs. chrome tanned ooze leather.)

10 lbs. Diamine Black BH
8 oz. Acid Violet
Run ½ hour, exhaust with
5 lbs. muriatic acid, and then drain off.
The skins are diazotized with,
10 lbs. muriatic acid. Run cold for 5 minutes, then add 5 lbs. sodium nitrite and run 15 minutes longer. Rinse thoroughly until there are no more nitrous fumes noticeable and develop with
1 lb. Phenylene Diamine powder dissolved with an equal amount of sal soda. Run 15 minutes, rinse and dye with
1 lb. of suitable Leather Black combination, after which the skins are lightly fat-liquored and dried.

Besides the above mentioned methods of dyeing, all of which in their many modifications are applicable to dyeing chamois leather, the use of the sulphur colors, known as Thion, Sulphogene, Immedial and Kategin colors are extensively used. The main reason for the use of these colors on chamois leather are, first, that the process has no deleterious effect on the oil tannage, and secondly, that they produce shades which though, not brilliant, are extremely fast to washing. Of course this quality is essential for this kind of washable leather. The dyestuffs of this class are mostly insoluble in water and must be dissolved with

equal quantities of sodium sulphide and dyestuff in boiling water. When the solution has cooled, one-fifth as much soap as of dyestuff is added, the volume of liquor brought up to the proper amount and then the skins are drummed in this solution for ½ hour, cold. They are then rinsed thoroughly and washed in warm water with 1 lb. of soap per 100 lbs. of skins. If the leather appears a little harsh a small quantity of egg yolk is added to the soap rinse. Where exceptional fastness to light and washing are required, an after-treatment with 1 lb. bichrome, 1 lb. bluestone and 3 lbs. acetic acid is given after the dyeing and before the fat-liquor treatment. When the skins are to be dyed on one side only, the color solution is made up in more concentrated form, brushed on the dry leather and then allowed to oxidize for 15 to 20 minutes after which they are thoroughly washed. All of the sulphur colors are suitable for this work, the choice being governed by the shade to be obtained. The sulphur colors which have the best solubility will be found to give the best results, while those colors which reduce in the dyebath should not be used as they do not fully reduce in a cold bath, the proper shade is not obtained and the results are very liable to be streaky.

TRANSPARENT LEATHER.

Since this is strictly an oil tannage the dyestuffs used for coloring must be soluble in oil. The coloring may be added directly to the oil used in tannage toward the end of the operation or the skins may be dyed in a fresh oil solution. This leather is also dyed by swabbing on the dissolved dyestuff.

Besides the oil colors, which are also known as Cerasine colors the following acid colors which are soluble in glycerine will be found to work very satisfactorily:—

For Yellow: Napthol Yellow, Azo Yellow.
For Orange: Orange II, Croceine Orange.
For Red: Fast Red A, Bordeaux BL, Azo Fuschsine.
For Violet: All brands of Acid Violet.
For Green: Napthol Green, Brilliant Milling Green B.
For Black: Napthol Blue Black, Alizarine Black.

These colors are dissolved, generally in the proportion of 1:100, and brushed on the raw hide.

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Bronze effects, also known as metallic colored leathers, are generally produced as follows: The skins are first dyed in the

tray or by brushing with a solution of some suitable basic color made up of about 1 oz. to 1 gal. of water. After dyeing they are rinsed and topped off with a solution of acid color made up of 2 oz. to the gallon. The leather is then set out from the flesh side, and the grain side slightly oiled with linseed oil and dried, then glazed. Another method to produce this leather is to dye it with a strong solution of basic color, oil off and dry. When dry it is glazed by the machine and then coated with a suitably colored collodium varnish which is diluted with amyl acetate and dried. This treatment may be repeated or the lustre may be increased by another glazing.

The following dyestuffs are suitable for this work:

Basic	Acid
Fuchsine	Fast Red A
Methylene Blue	Brilliant Croceine
Methyl Violet	Acid Violet
Malachite Green	Napthol Green
Brilliant Green	Orange II
Safranine	Brilliant Milling Blue B
Bismarck Brown	

There are a great many methods of producing marbled or antique leather, and, as will be seen by the processes described, the possibility for originality in their production is unlimited. The sides to be tanned are tied up in bags and immersed in strong tanning liquor which puckers up the leather quickly and does not reach completely into the crevices where the leather is folded. After this operation the sides are removed from the bags and the tannage completed. The irregular raised portions produced are absolutely permanent. Another method of producing the same result is to apply wooden clamps to the flesh side of the skins while in the first tanning liquor and to remove them for the final tannage. Still another method and the one more often used for cheaper leather is to emboss the pattern by means of an engraved roller after the bottom color has been applied. For the dyeing proper the skins are dyed in the tray in pairs with either acid or basic colors and then oiled off slightly and dried. When dry the raised portion of the grain may be colored with a solution of color dissolved in collodium varnish or the raised portions resisted by brushing over a fatty resist made up of wax and vaseline

and the other parts dyed with a suitable solution of basic color. Still another method is to bottom dye with acid colors which have very good penetrating powers and then to top dye with basic colors which mainly dye the surface. When dry the raised portions are buffed off and the acid color shows through. The limit to the number of combinations possible is entirely dependent upon the ingenuity of the dyer.

Glaze Finishes are prepared by soaking albumen in water; egg albumen for colors and blood albumen for black, and then adding a small amount of gelatine to the mixture and bringing the solution up to the right consistency with water. Enough dyestuff is added to the finish to slightly color it except for black, and in this case the finish is rather strongly colored. It is brushed on the leather and when dry is glazed on the machine.

The following list of colors will be found suitable:—

For Yellow: Azo Yellow.
For Red: Croceine Scarlet
Fast-Red A.
Browns: Resorcine Brown.
For Blue: Napthol Blue.
For Green: Acid Green.
For Black: Nigrosine W.S.

Protective Finishes:—Under this head come finishes which are to protect the leather from outside influences such as rubbing off in the case of upholstery and saddle leather. For this any of the following solutions are suitable and should be colored only enough to prevent a white cast on the leather due to the finish.

Collodium Varnish:—This is a solution of nitrocellulose in amyl acetate colored with suitable combinations of the oil-soluble colors which are dissolved in the varnish by agitating. Very often castor oil is added to this finish to give elasticity to the finish. As many coats as necessary are applied.

Shellac Solution in Alcohol:—This solution is prepared by dissolving the proper amount of shellac in alcohol and coloring with any of the basic colors depending upon the shade of the leather to be finished. Part of the alcohol may be replaced by turpentine. In place of the alcohol used as a solvent for the shellac, borax and ammonia may also be used in which case the basic colors are first dissolved in water before being added to the finish.

CONTRIBUTION FROM AMERICAN RESEARCH LABORATORY. GUYACAN.

By G. L. Terrasse and J. F. Anthes.

Rec'd Oct. 28, 1919.

A relatively new source of tannin is always of interest to leather chemistry irrespective of its commercial aspects, and in the case of the seed pods of the Guyacán there already seems to be some local utilization of these pods as a tanning agent and they may become of moment in the various trade routes if their price is not prohibitive.

I.—*Botany of Guyacán.*—The undersized tree belongs to the family *Leguminosae,* is hence a phanerogamic dicotyledon, and specifically is known as *Caesalpinia melanocarpa, Griseb.* The tree or large shrub has tapering, cylindrical stems and branches which are spineless; has a pubescent petiolation and glabrous foliage. There is a solitary gland in each petiole and petiolule.

Leafage is bi- and imparipinnate and each main pinna is composed of four pairs, or less often of three pairs, of secondary pinnae and each secondary pinna is made up of from eight to ten pairs of ovate-oblong leaflets, smooth on both sides and about 2 cm. long. The inflorescence apparently has not been well studied.

The stipitate, pruniformic legume is somewhat woody, ovoid-oblong, and compressed dorsi-ventrally. It is about 10-15 cm. long, 8 cm. broad, and 4 cm. thick, convex on both sides, with rounded margins. The pod has three or four flattened seeds separated from each other by cellulosic partitions.

The tree is rather small with crooked, spreading branches and its wood is classed as hard and straight grained. Perhaps it is the same species as *Caesalpinia fimbriata, Tul. boliviana,* whose legume is not yet well studied. The genus is poorly defined; and each pedicel of the corymb of the *melanocorpa* is one flowered, thus differing from the *Mimosae.* It is not found in thick stands, in either fields or woods, but isolated in subtropical Argentina (Tucuman). Guyacán is also spelled locally Guaycán and Quajacan.

II. *Chemistry of Guyacán.*—An analysis of a ground sample of the pods by the official method of the A. L. C. A. follows:—

	As Received	Dry Basis
Water	11.40%	
Insolubles	0.76	0.86%
Non-Tannins	37.21	42.00
Tannin	22.53	25.43
Non-Extractive	28.10	31.71
Total	100.00%	100.00%

	As Received	Dry Basis
Copper reducing material, after inversion of aqueous extractive, calculated as glucose	21.1%	23.8%
Copper reducing material, after inversion of original ground pods, calculated as glucose	32.7%	36.9%

Guayacán resembles among the commoner tanning agents Divi Divi *(Caesalpinia coriaria)*. Its tan content is distinctly lower than Divi Divi's and the purity of its aqueous extractive (tannin divided by total extractive), 37.2, is likewise low. The insolubles in the aqueous extract are low and an inspection of the non-extractive shows translucent, gummy flocks. The color of the finished leather is a pale yellow inclining to a brown; the leather is distinctly plump, soft and pliable. The total sugar forming and formed material is high, 36.9% on a dry basis, and presumably largely available as an acid producer in tanning. It seems probable from the sugar content of the water soluble that a large percentage of the total available invert sugar content is ready formed sugar. No determinations were made of the ready formed sugar in the pod and the percentage of this fermentable; the per cent. sugar fermentable of the inverted aqueous extractive; and the per cent. fermentable of the inverted ground pods.

The tannin gives blue-blacks with iron-alum and hence is not a pure catechol tan; bromine water produces no precipitate in aqueous infusion; the evidence thus favors the assumption of pure pyrogallol tannin.

ABSTRACTS.

Tanning School of the Tanners' Council. At the Annual Meeting of the Tanners' Council of the U. S. A. held in Chicago on October 16-17 the Chairman of the Committee on the Tanning School presented the following recommendations:

(1) The tanning school should be located in New York City.

(2) The school should be under the control of a director appointed by and responsible to a Committee of Administration, consisting of representatives from both the tanning and allied industries.

(3) Plans of organization of the courses of instruction should provide for such instruction in addition to tanning practice as will tend to qualify the young men for future development in the direction of tannery superintendency.

(4) A post-graduate course in leather chemistry designed to afford special training for young men who have already acquired a comprehensive high-grade technical course in chemistry should also be provided in accordance with entrance requirements.

(5) In order that the industry may at all times be able to absorb the graduates of the school, the number of students enrolled each year should not exceed thirty.

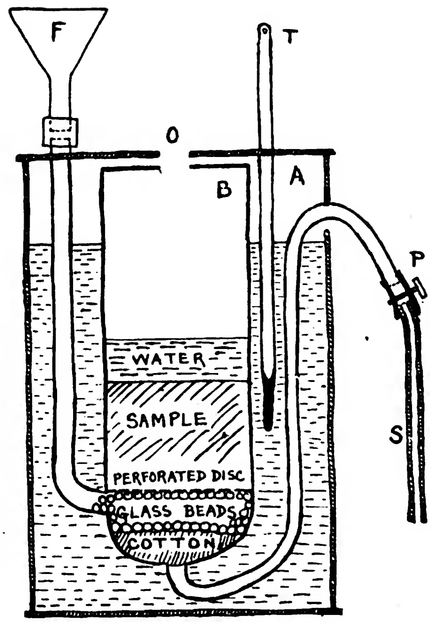
(6) To adequately provide for the instruction of the number of students referred to in the preceding paragraph, it is estimated that a capital of not less than $1,000,000 will be required. One-half of this sum would be considered as capital to be used in building up the school and the remainder would constitute an endowment fund, the interest from which would defray the major part of the expense of maintaining the institution.

(7) The committee recommends that the American Leather Research Laboratory be co-ordinated with the proposed tanning school.

(8) Entrance requirements should be the following:
- Minimum age of 18 years.
- Character should be vouched for by satisfactory references.
- Not less than one year's practical experience—of an approved character—in a tannery; experience to be vouched for by the employer.
- A reasonable minimum command of English and arithmetic.

These eight points have been embodied into a prospectus which has been distributed to the members of the campaign committee to use in connection with the work of raising funds for the school.

Some Tanning Materials of the French Colonies; Their Analysis and Identification. By M. E. Jalade, *Le Cuir* 8, 219 and 277 (1919). A detailed description is given of the official method for analysis of tanning materials of the International Association of Leather Trades Chemists. In the extraction of soluble matter from ground barks, etc., Jalade finds the Koch extractor cumbersome and inconvenient to fill and, working under a pressure of two meters of water, it responds imperfectly to the purpose in view. As for the Procter extractor, it is fragile and not always readily replaceable. Jalade has therefore designed an apparatus which he believes overcomes the objectionable features of the other types. This extractor is shown in the figure.



JALADE EXTRACTOR
(TIN-LINED COPPER)

Fig. 1.

The extractor B is suspended in the water bath A, which is kept heated to the desired temperature by a Bunsen burner. The outlet of the extractor is plugged with cotton covered with glass beads. On the top of the beads is placed a perforated disc for holding the powdered sample. For intermittent extraction, distilled water is run in through the funnel F with cock P closed; at intervals P is opened and the extract siphoned through tube S into the receiving flask. For continuous extraction, water is dropped, by any suitable device, through the opening O directly onto the sample, P being regulated so that the sample is always submerged. For any given material, the apparatus must be so operated as to insure complete extraction with the amount of sample and water required by the official method.

In the exploitation of new tanning materials, it is important to be able to recognize each of the materials available. This can be done by testing for characteristics prominent in some materials while scarcely discernable in others. Jalade points out that the tests he recommends are only for identifying pure materials and not at all for the detection of adulterants in mixtures.

Certain materials, notably mangrove, contain tannin anhydrides only slightly soluble at room temperature. These can be detected by watching

the liquor during the extraction. The anhydrides are dissolved by the hot water, but readily crystallize upon even a slight cooling.

A common means of identifying groups of tannins is by testing for pyrogallol and catechol tannins. The catechol tannins are precipitated from a hot solution by addition of a mixture of formaldehyde and hydrochloric acid, and can be filtered off. The test for pyrogallol tannins is then made by adding iron alum to the filtrate after addition of an excess of sodium acetate. Or the pyrogallol tannins may be precipitated first by making the solution slightly acid with acetic and adding neutral lead acetate solution. A pure material can thus be placed into one of three groups, since some materials contain only catechol tannins, others only pyrogallol, and still others contain both kinds.

A very valuable means of identification is the Mülhausen test, the principle of which is that each kind of tannin forms a differently colored lake with certain metallic salts. A strip of calico is first mordanted with the salt, such as of iron or aluminum, and then put into a boiling solution of the tan liquor. The colors are examined after drying the strips. The exact shades produced depend very much upon the physical conditions of the tests, so it is essential to make all tests under rigidly identical conditions. Where two kinds of tannins are present, the color due to the pyrogallol tannins usually predominates.

Jalade finds Schell's reaction for mangrove entirely unsatisfactory, since the test gives as much difference between the several kinds of mangrove as between quebracho, mimosa, and others.

The amount of ash and its chloride content vary so much in different materials that these determinations are of some value in identifying an unknown material.

Analyses of different types of mimosa, mangrove, and materials of African origin are appended.

J. A. W.

The Present State of Our Knowledge of the Qualitative Analysis of Common Tanning Extracts. By E. SCHELL, *Le Cuir* **8**, 236 (1919). Coöperative study of this delicate subject has been stopped by the long period of war; in fact very little advancement has been made since the publication of Stiasny's work in 1911 and 1912. While it may be easy to detect gross frauds, such as adulteration, or to recognize a pure extract, great uncertainty still exists in the determination of what and how much of various tanning extracts are contained in even only slightly complicated mixtures. Although numerous data are available, we cannot, with our present knowledge, outline any rigid procedure for the qualitative analysis of tanning extracts, since wide experience is necessary to judge appearances of solutions and precipitates, odors, tastes, etc., and to interpret results. But, for persons familiar with the properties of the common extracts, the following steps will prove to be valuable guides:

1. Regular analysis by the Official Method, paying particular attention to the examination of total solids, soluble matter, and non-tans.

2. Examination of tan liquor with tintometer, such as that of Lovibond.
3. Determination and complete analysis of the ash.
4. Tests for common adulterants, such as sulfite cellulose with Procter-Hirst reaction.
5. Separate catechol from pyrogallol tannins, estimating the amount of each.
6. Determine solubility of extract in various organic solvents, such as ether, alcohol, etc.
7. Observe tanning and coloring properties of tan liquor on pieces of pelt preserved in boro-phenol.
8. Make Mülhausen test (see preceding abstract) using as mordants, salts of Al, Fe, Sn, Co, Ni, Ce, U, and Cr.

The next step is to verify by all special tests known any conclusions which may have been drawn from the above tests, which are not in themselves absolutely conclusive. The amount of catechol tannins is determined by adding to the tan liquor a mixture of formaldehyde and HCl, filtering, and washing, drying and weighing the precipitate; but this determination is valuable only as an approximation, since the precipitation, as in the case of sumac, is not always complete. If the proportions used in the Procter-Hirst reaction are not exactly right, the reaction may be sluggish. Often the examination of the ash may reveal nothing or even be misleading, since it may have had its origin, not in the tanning material, but in the water used in extraction or in added chemicals. All comparative tests must be made under absolutely identical conditions or they may lead to false conclusions. All precipitates should be carefully studied under the microscope.

Since we have not made further progress by chemical means, recourse should be had to physical apparatus, possibly to the spectroscope, electrical conductivity apparatus, dialyzers, and others. Our future technical laboratories should be equipped with apparatus now confined chiefly to universities.

J. A. W.

Procedure for Determining the Degree of Clarification of a Chestnut Extract. By E. SCHELL, *Le Cuir* **8,** 242 (1919). Depending upon the method of extraction, ordinary chestnut extract contains more or less of certain gummy or resinous substances, which increase the viscosity and may prove a source of annoyance in the tannery by adhering to the surface of the skins and retarding the penetration of tannins. This trouble is greatly lessened by subjecting the extract to a clarification process which renders the extract more fluid, lighter in color, and less likely to mould. The degree of clarification is determined by noting, during analysis by the Official Method, the rate of filtration of both the initial and non-tannin solutions, and by carefully examining the filtrates for a slight opalescence or turbidity that does not disappear on standing. With an unclarified extract, the filter paper becomes gummed up before the first 250 cc. have passed through and the remaining liquor filters very slowly; moreover, the

filtrate is never optically clear. A well clarified extract filters quickly and gives a clear filtrate. The rate of filtration can be taken as a comparative measure of the degree of clarification.

J. A. W.

Application of Oils and Greases to Leather. By J. R. Blockey, *Shoe & Lea. Rep.*, July 18 1918 *et seq.* The use of oils in leather making dates back to ancient times. The modern method of manufacturing chamois leather is a close parellel of the ancient use of oil. Only highly unsaturated fatty oils such as cod oil, that are capable of undergoing the desired chemical changes are suitable for a straight oil tannage. The effect produced in a true oil tannage takes place to a certain extent in the other processes in which oil is applied to a mineral or vegetable tannage. In the oiling of the grain of tanned leather before drying a certain combination takes place between the oil and the leather. The object of applying oil to the grain of tanned leather before drying, apart from the slight oil tannage, is to maintain a better color and to produce a grain that will not crack by preventing oxidation and reducing evaporation from the grain side to a minimum. These effects are more pronounced in leathers containing a large proportion of "unfixed" tanning matter and is almost negligible in leathers containing none or only a very small quantity. Oil or grease applied to dry leather darkens its color which is caused by the oil forming a continuous film on the surface and presenting a smaller surface to the light. Consequently the reflection of light rays is decreased and the color appears darker. The tensile strength of the leather is increased by oiling and stuffing. As the amount of grease is increased, as a general rule, the tensile strength increases. This effect is due largely to lubrication and the separation of the fibers. To obtain the maximum increase in tensile strength it is essential that the oil or grease be absorbed by the leather in the wet state.

"Cracky" grain can be improved or remedied by oiling if it is not caused by the thickness of the leather or by being too dry. It is obvious that the thicker the leather the greater the strain which the grain will have to stand when the leather is bent, and by removing a small proportion of the moisture the surface of the leather becomes more brittle. One method of removing the tendency to crack is by buffing. By removing a very thin shaving from the grain of the leather it is often possible to prevent cracking.

Hand stuffing differs from oiling of the grain in that instead of liquid a paste or dubbin is applied. The dubbin is applied by brushing on the wet leather, giving some parts more than others if necessary, and then hanging up to dry. Only the liquid portion of the dubbin is absorbed by the leather, the solid portion being left on the outside and this is slicked off after the leather is dry. Larger amounts of oil can be incorporated in the leather in one application by hand stuffing than by oiling. The most common dubbin is a mixture of equal parts of cod oil and tallow.

Drum stuffing consists of churning the damp leather in a drum with oil or melted greases. By drum stuffing greases or waxes may be taken

up by the leather which at ordinary temperatures are solids. It is obvious if grease can be absorbed by the leather very much larger quantities can be taken up without the leather becoming greasy to the feel. The drums are capable of being heated by hot air heating devices, to the temperature desired. The leather is then put into the drum and after it has been in long enough to come to the desired temperature the melted grease is added and the drum is rotated until the grease is absorbed. The temperature must be high enough to keep the grease fluid and the maximum temperature is set by the leather to be treated. Most vegetable tanned leathers while moist will withstand a temperature of 120° F., while some will begin to be scalded at 150° and the majority of well-tanned leathers will not begin to perish until 160° F. is attained. Dry leather will withstand a much higher temperature and the dryer the leather the more resistant it is to heat. Chrome tanned leather will withstand a very much higher temperature than vegetable tanned leather both in the wet and dry state therefore a much higher temperature can be used for it in stuffing.

The advantages drum stuffing offers over hand stuffing are:—Saving of time and labor, ease of control giving more uniform color and quantity of grease, more economical use of the grease, larger quantities of grease can be absorbed and consequently the leathers will be more waterproof. The factors which govern the amount of grease which can be absorbed by leather are; the amount of moisture it contains, the condition of the leather, that is, whether it is compact or otherwise, the temperature that can be used, and the hardness of the grease employed.

In the Dipping process of impregnating leather with grease, the leather is dried and then immersed in melted grease. The dipping is done at a higher temperature than is drum stuffing, that is, harder greases are used. If the leather is dried in a hot drying room at 45° it is quite safe to dip it in melted grease at a temperature of 85-90° C., providing the leather is well tanned. The time of the immersion of the leather depends upon the amount of grease it is desired to have in the leather. After the leather is taken out of the grease it is usually soaked back in water which is carried out in the drum. The mechanical action of the drum helps to soften the leather and separate the fibers otherwise the tensile strength and other properties are not as good.

The Burning-in process differs from the dipping process in that the melted grease is applied to the dry leather on a table instead of by immersion. The hot melted grease is poured on to the flesh side and brushed in. After being impregnated with grease in this manner, the leather is finished the same as that treated by the dipping process. The advantages the burning-in process offers over the dipping process are:—a better color may be obtained, definite quantities of grease may be incorporated and the grease mixture may be varied for different parts of the leather. On the other hand the dipping process is easier to manipulate, temperature can be easily regulated and is more economical of time and labor.

The production of japanned, patent or enamelled leather depended entirely upon the application of certain drying oils, principally linseed oil

before the advent of soluble cotton varnishes. A varnish is made of boiled linseed oil, certain "driers" and the necessary pigment. The leather having been thoroughly set out, to remove all stretch, dried and degreased is given the first coat of varnish, transferred to the stove with little application of heat and when dry the surface is made smooth by rubbing with pumice stone. A second and thinner coat is then applied and dried at a slightly higher temperature. The surface is again pumiced and a third and final coat of varnish is applied. This is then dried in a very hot stove and finally in the open air.

Fat liquoring is merely a process of applying oil to leather in the form of an emulsion. The wet leather is drummed in an emulsion of a suitable oil and water stabilized by the use of soap or sulphated oil. In the use of soap for this purpose soft soap is better than a hard soap and in either case it is recommended that just enough soap be used to emulsify the oil so as to form a permanent emulsion. Fat liquoring gives a soft flexible leather and by this means it is possible to incorporate more oil in the leather without giving it a greasy feel.

The fat liquoring of colored leather is a more delicate operation and is carried out either before or after dyeing. When fat liquoring before dyeing the whole of the emulsion must be taken up by the leather and the surface must be free from grease so that the goods will dye evenly. One of the principle difficulties in fat liquoring after dyeing is the stripping of the dye by the fat liquor, and in order to overcome this it is recommended that the fat liquor be added to a little of the partially exhausted dye bath.

Sulphonated or sulphated oils have the great advantage over soap, when used to prepare fat liquors, in that a slight acidity does not break the emulsion and deposit fatty acids on the outside of the leather and thereby give it a greasy feel. Then sulphonated oils may be used to great advantage in fat liquoring chrome leather which is always acid in character after tanning. It is also possible, when using sulphonated oil in the fat liquor, to dye and fat liquor in one operation.

Sulphonated oils either alone or in conjunction with mineral oil are largely used in ordinary drum vegetable tanning, to help the tanning material to penetrate faster and also to prevent damage to the grain of the leather by the action of the drum. It also helps to prevent crackiness and brittleness.

Amides of the fatty acids, such as stearamide, are also used as emulsifying agents. Commercial fat liquors are now on the market made with stearamide as the base.

G. W. S.

The Direct Transition from Tanning Liquors into Powdered, Solid Extract of Low Water Content. By PROFS. SMAIC and WLADIKA, *Gerber* **45**, 189, 205 (1919). While liquid extracts are more resistant to decomposition by fermentation and chemical rearrangement than tan liquors, solid extracts are more so. In general the lower the water content of a tanning extract the more stable it is.

In fluid or solid extract the time for concentration and the tempera-

ture must be reduced to a minimum, for, as is known, a relatively low temperature if held for any length of time, even in a vacuum produces decomposition. The ideal transition of tan liquor into solid extract without any heat can be accomplished by a method advanced recently which was originally used for the drying of milk, albumin, gelatine, etc. The liquor to be dried is finely sprayed or atomized in the cold state by means of compressed air through nozzles into a closed chamber and the water vapor is continually sucked away. The dried material collects on the sloping bottom of the chamber in the form of a powder and can be removed automatically. An oakwood liquor of 8.6° Bé was converted into a powdered solid extract. The analysis (By shake method) before and after was as follows:—

	8.6° Liquor	Solid Extract	Liquor calculated to Extract basis
Tannin	9.12%	50.54%	50.94%
Non-tannin	6.99	39.91	39.04
Water	83.45	7.58	7.58
Insolubles	0.44	1.97	2.45
Ash	0.66	3.30	3.68

Taking into consideration the difficulty of obtaining an absolutely homogeneous sample and the unavoidable errors always inherent in a conventional method, the analyses show that there is no change in the constituents of the liquor. Especially that there has been no oxidation of the tannin in spite of being conducted in a large excess of atmospheric oxygen. This was also verified by the fact that the color of the extract, when diluted back to the original liquor, remained unchanged.

The following analysis of a dry, powdered sulphite-cellulose extract made by this process, is given to show the low water content that is easily obtained.

(By shake method)

Material removed by hide	44.91%
Material not removed by hide	48.63
Water	6.46
Insolubles	0.00
Ash	11.59

The powdered extracts made by this process, in consequence of their low water content are not hygroscopic and therefore do not agglomerate.

As it is recognized that even different liquors coming from the same source may behave differently in the process of drying, it is recommended that more of various kinds of liquors be converted into dry powdered extract by this process in order to substantiate the results already obtained.

G. W. S.

Automobile Tire Leather. *Ledertechnishe Rundshau* thru *Gerber-Courier,* Sept. 27, 1919. Automobile non-slip leather must possess softness, a certain elasticity, capability of resisting, and, in order that it may be united with the tire gum by vulcanization at a temperature of 60° C., must possess a suitably great heat resisting quality. The last property can be

obtained by a chrome tannage. Such a leather must, however, contain a larger quantity of sulphur so that the rubber cement will take a better hold on it.

In the tanning therefore there are two factors to be considered; a preliminary tannage, with consecutive treatment of the pelt with solutions of sodium thiosulphate (antichlor) and acid, so that a sufficient quantity of sulphur is deposited in the pelt (sulphur tannage) and an after tannage with chrome. Steer or buffalo hides are suitable, the latter being the better. The hides are soaked in a solution of sodium sulphide, limed, etc., if necessary leveled and then cropped. For the sulphur tannage, to 100 kilograms of pelt first 12%, and then 8% of antichlor is used and for the acid bath to every 100 liters of water 8 kilograms of hydrochloric acid and 24 kilograms of common salt. The antichlor is given in the fuller, the acid bath in the handler.

The chrome tannage is carried out according to the one bath process. A suitable chrome liquor is obtained if, to a solution of 10 parts of chrome alum in hot water, 1 part of whiting is added and the precipitate of gypsum allowed to settle. Usually a series of six liquors are maintained with the highest at 35° Bk., the hides staying in each liquor two days. The first liquor of the series serves as a plumping liquor, is exhausted to 12° and then made up to 28-35° with fresh chrome liquor and used as the last liquor. The chrome tannage may be carried out in the vats but then it must receive first a weak liquor in the handlers to serve as a plumping liquor.

An especially soft and white automobile leather is obtained if chrome and aluminium salts are used together for the tannage. Eight parts of chrome alum and 2 parts aluminum sulphate is dissolved in 50 parts of water and the solution made basic with the addition of 1 part of whiting. The resulting solution is then used in the same manner as given above. After tanning the leather is struck out on the jack, let lay 2 hours, washed with water and then fleshed. The customary after-leveling is omitted for leather made with sulphur tannage. The leather should contain none or only a limited amount of fat, so that its capability to vulcanize is not injured. It must however be fat liquored in order to obtain the desired softness and flexibility. The fat liquor used differs from that usually used on chrome leather by containing not an excess of fat but an excess of soda. This is best prepared with castor oil soap with some soda. If the leather is to possess an especialy white color then french chalk is added to the fat liquor. The fat liquored crops are rinsed, stretched and dried on the table or in the frames. The dried leather is left to absorb moisture in a moist room. Then it is set-out on the setting out machine, dried again, re-setout and finally powdered over with lithopone to enhance the white color.

G. W. S.

Contribution to the Purification of Tannery Sewage. ANON, *Gerber* **45**, 245. Primarily a presentation of German patent No. 303040 by Carl Gunkel of May 1, 1915 in which it is claimed that all kinds of sewage is

purified and deodorized by a treatment taking place in three phases: (1) A solution of potassium chloride or sulphate, or of magnesium chloride or sulphate is first mixed with the sewage and allowed to stand ½ hour to settle. Potash tailings (the residue from the manufacture of potassium sulphate which contains principally magnesium chloride and sulphate and some potassium chloride) may be used also. After settling the supernatant liquid is run off into another sedimentation basin, and (2) there is added to it a thin paste of a mixture of highly plastic clay and siliceous mineral fragments. This mixture is left to stand one hour when the supernatant liquid is drawn off into a third basin and there is added to it (3) a mixture of the above mentioned clay paste and milk of lime. The precipitate formed settles rapidly and the purified sewage will be colorless and odorless.

Experiments were run on a bark tannery effluent containing the waters from the soaks, bates and drenches, and old tan liquors. The beam house liquors were not contained in it.

Analysis of Sewage before treatment	mmg/liter	Analysis after treatment mmg/liter	Per cent. removed
Residue on evaporation at 110° C. ...	6080	2412	60.3
Insoluble matter	1276	18	98.6
Insoluble mineral matter	280	6	97.8
Insoluble organic matter	996	12	98.8
Total soluble matter	4804	2394	50.2
Total soluble mineral matter	1920	1495	22.0
Total soluble organic matter	2884	899	68.8
Total nitrogen	190	51	73.2
Total mineral matter	2200	1501	31.8
Total organic matter	3880	911	76.5

The sewage was originaly strongly turbid, dark yellowish brown, of repulsive putrid odor and contained a large amount of suspended matter. The purified water was clear, very slightly colored, of very faint odor and contained only a trace of suspended matter.

It is claimed that municipal sewages may be treated satisfactorily with the mixture of highly plastic clay alone. But the preliminary treatment with salt solution and the after treatment with the mixture of clay slime and lime is necessary for effluents from textile factories and the like.

G. W. S.
